

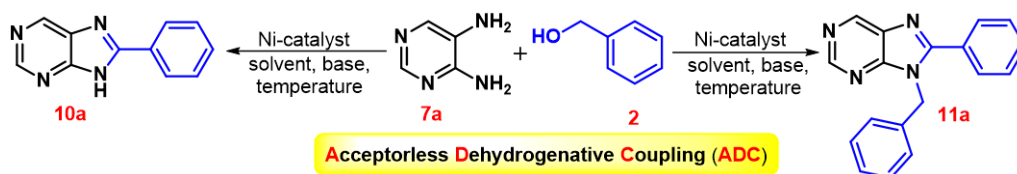
# **Nickel catalyzed sustainable synthesis of benzazoles and purines via acceptorless dehydrogenative coupling and borrowing hydrogen approach**

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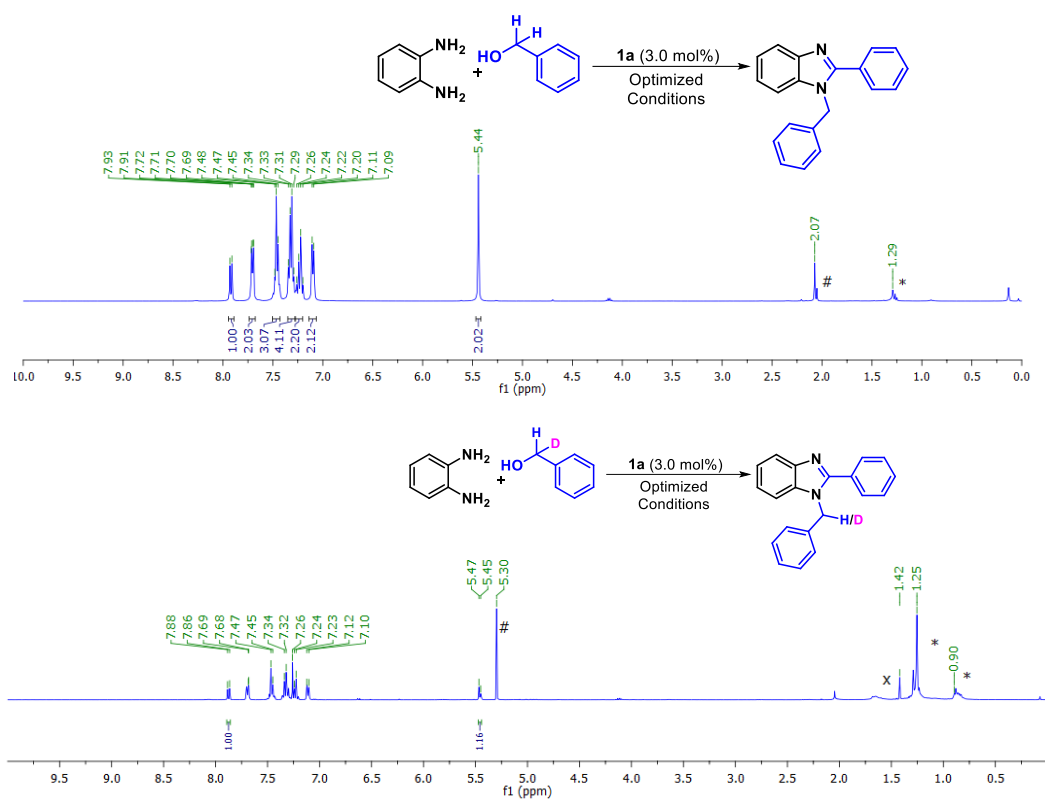
**Table S1.** Optimization of Reaction Conditions for 8-Substituted-9*H*-purines and 8,9-disubstituted-9*H*-purines <sup>a-f</sup>.



Entry	Ni- Catalyst (mol%)	Solvent	Base	Temp. (°C)	Yield (%)	
					Purines	
					<b>10a</b>	<b>11a</b>
1	<b>1a</b> (3.0)	toluene	KO <sup>t</sup> Bu	100°C	70	45
2	<b>1a</b> (3.0)	toluene	NaO <sup>t</sup> Bu	100°C	59	35
3	<b>1a</b> (3.0)	toluene	KOH	100°C	53	32
4	<b>1a</b> (3.0)	toluene	K <sub>3</sub> PO <sub>4</sub>	100°C	NR	NR
5	<b>1a</b> (3.0)	toluene	NEt <sub>3</sub>	100°C	NR	NR
6	<b>1a</b> (3.0)	xylene	KO <sup>t</sup> Bu	100°C	67	41
7	<b>1a</b> (3.0)	THF	KO <sup>t</sup> Bu	100°C	trace	trace
8	<b>1a</b> (3.0)	ethanol	KO <sup>t</sup> Bu	100°C	NR	NR
9	<b>1a</b> (3.0)	xylene	KO <sup>t</sup> Bu	120°C	57	51
10	<b>1a</b> (3.0)	xylene	KO <sup>t</sup> Bu	140°C	42	39
11	<b>1a</b> (3.0)	toluene	KO <sup>t</sup> Bu	100°C	68 <sup>d</sup>	NR <sup>d</sup>
12	<b>1b</b> (3.0)	toluene	KO <sup>t</sup> Bu	100°C	34	-
13	<b>1a</b> (3.0)	xylene	KO <sup>t</sup> Bu	120°C	-	23
14	-	xylene	KO <sup>t</sup> Bu	120°C	trace	trace
15	<b>1a</b> (3.0)	xylene	-	120°C	NR	NR
16	NiCl <sub>2</sub> (10.0)	xylene	KO <sup>t</sup> Bu	120°C	NR	NR
17	Ni(OAc) <sub>2</sub> (10.0)	xylene	KO <sup>t</sup> Bu	120°C	NR	NR
18	NiCl <sub>2</sub> (3.0) + DME	xylene	KO <sup>t</sup> Bu	120°C	trace	trace
19	NiCl <sub>2</sub> (3.0) + P(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	xylene	KO <sup>t</sup> Bu	120°C	trace	trace

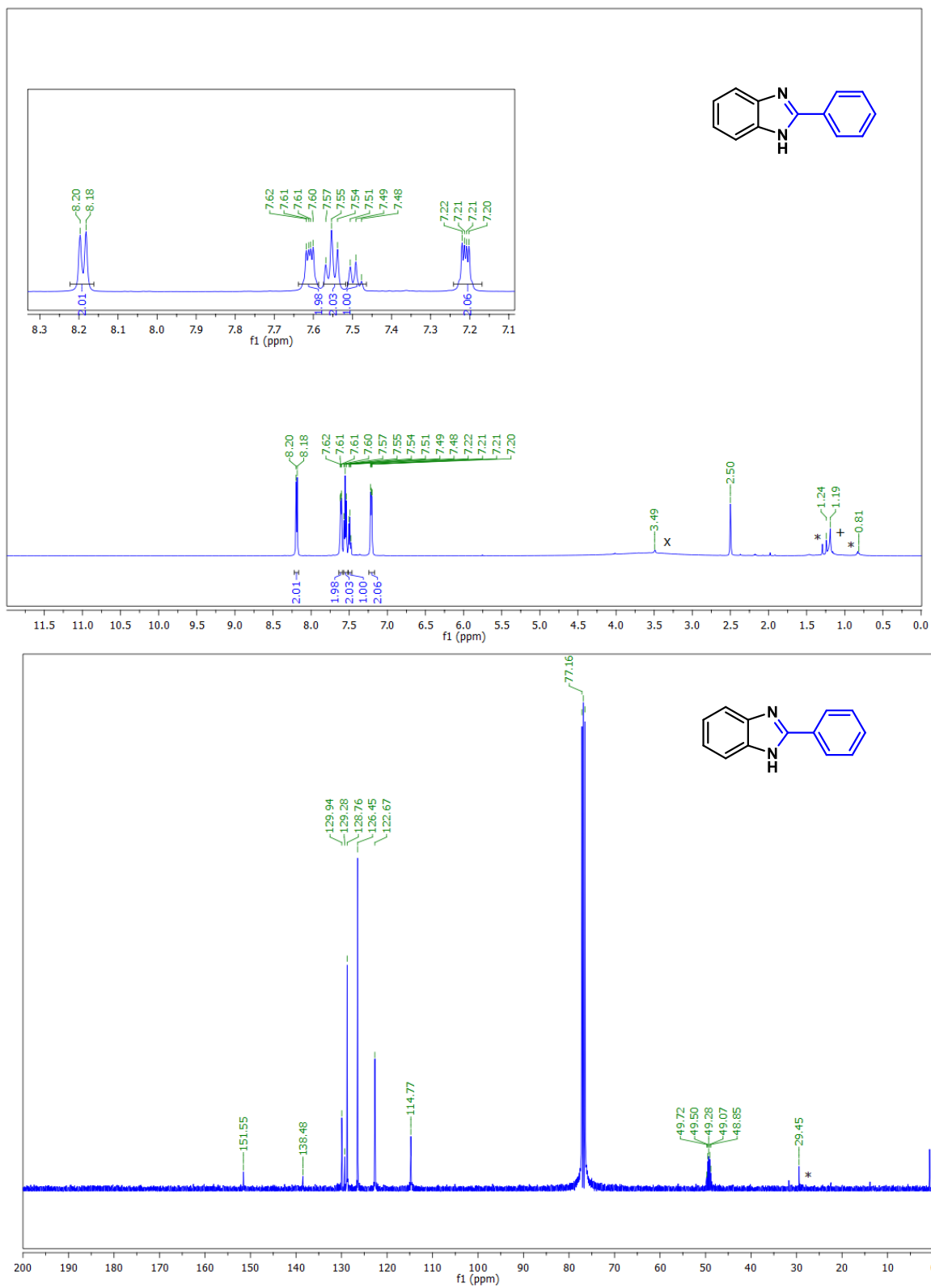
For **10a**. <sup>a</sup>Stoichiometry: benzylalcohol (**2a**) (1.0 mmol), 4,5-diaminopyrimidine (**7a**) (1.0 mmol), base (0.75 mmol); <sup>b</sup>Solvent: 5.0 mL; <sup>c</sup>Under argon atmosphere; <sup>d</sup>Under aerobic condition; <sup>e</sup>Time: 24h; <sup>f</sup>Isolated yield after column chromatography.  
 For **11a**. <sup>a</sup>Stoichiometry: benzylalcohol (**2a**) (2.0 mmol), 4,5-diaminopyrimidine (**7a**) (1.0 mmol), base (2.0 mmol); <sup>b</sup>Solvent: 5.0 mL; <sup>c</sup>Under argon atmosphere; <sup>d</sup>Under aerial condition; <sup>e</sup>Time: 36h; <sup>f</sup>Isolated yield after column chromatography.

## Deuterium Labelling Experiment.

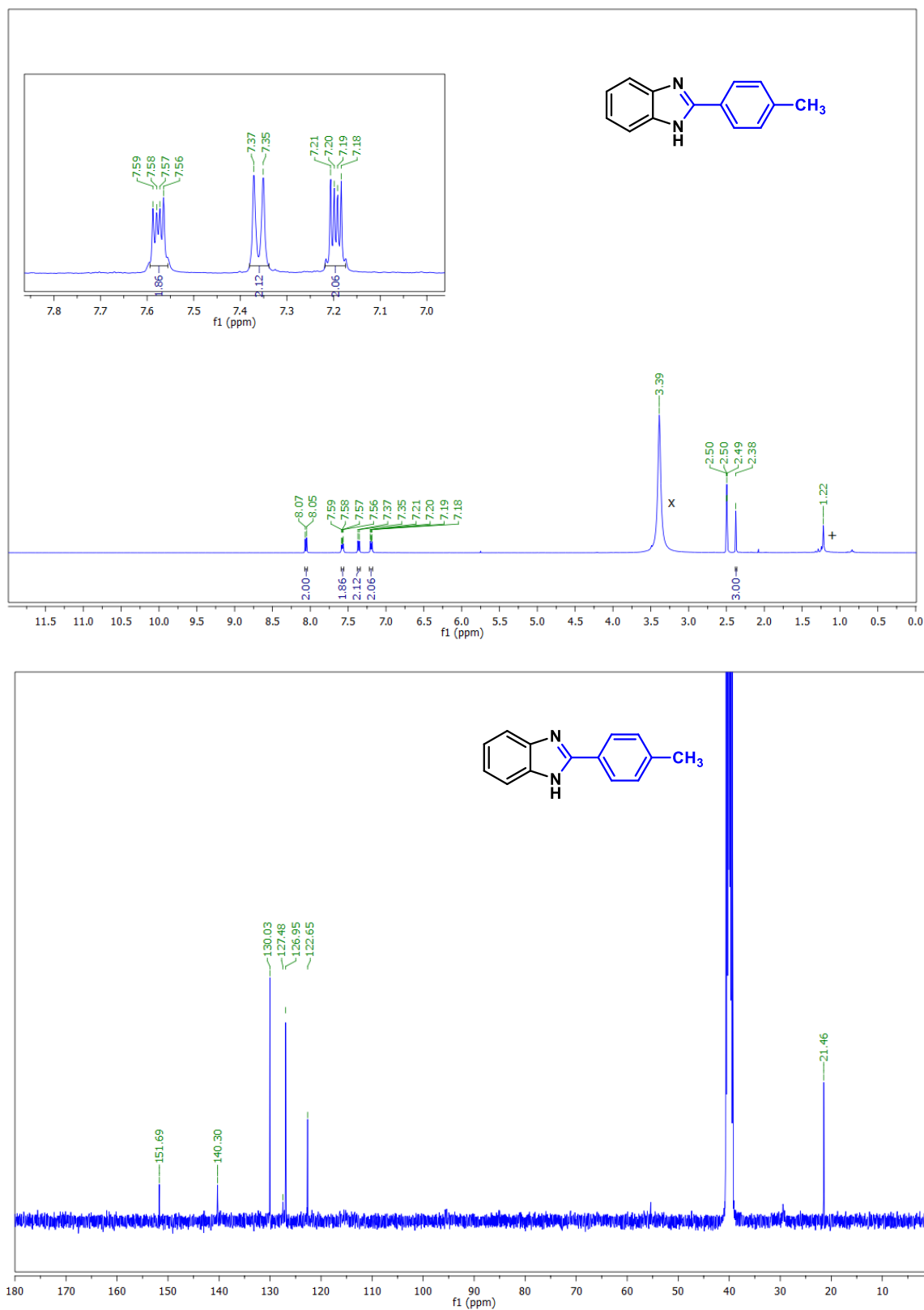


**Fig S1.**  $^1\text{H}$  NMR spectra of **8a** and **8a-d** in  $\text{CDCl}_3$  solvent (#dichloromethane,  $^x$ water,  $^*$ hexane)

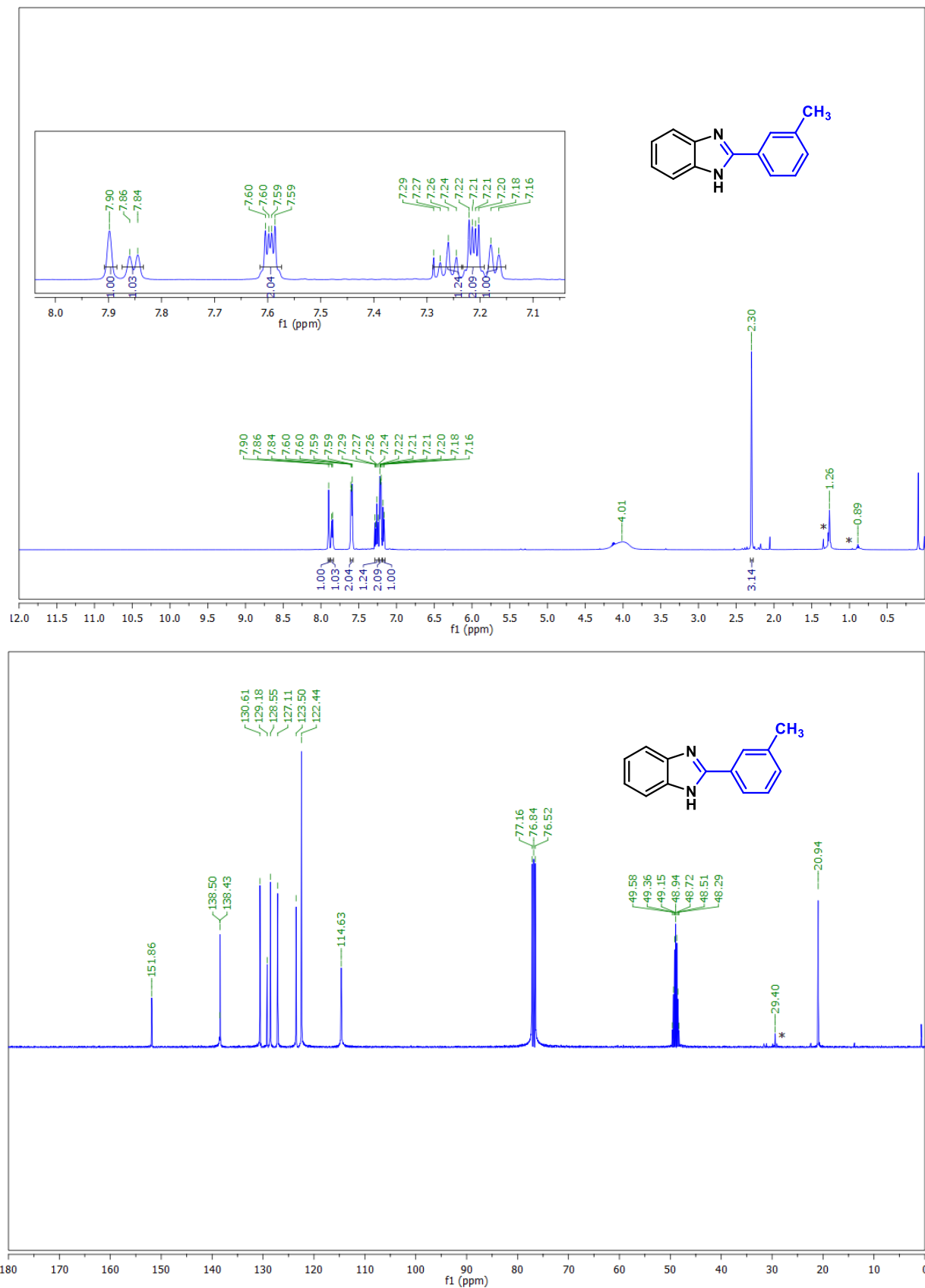
## Figures of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Isolated Compounds.



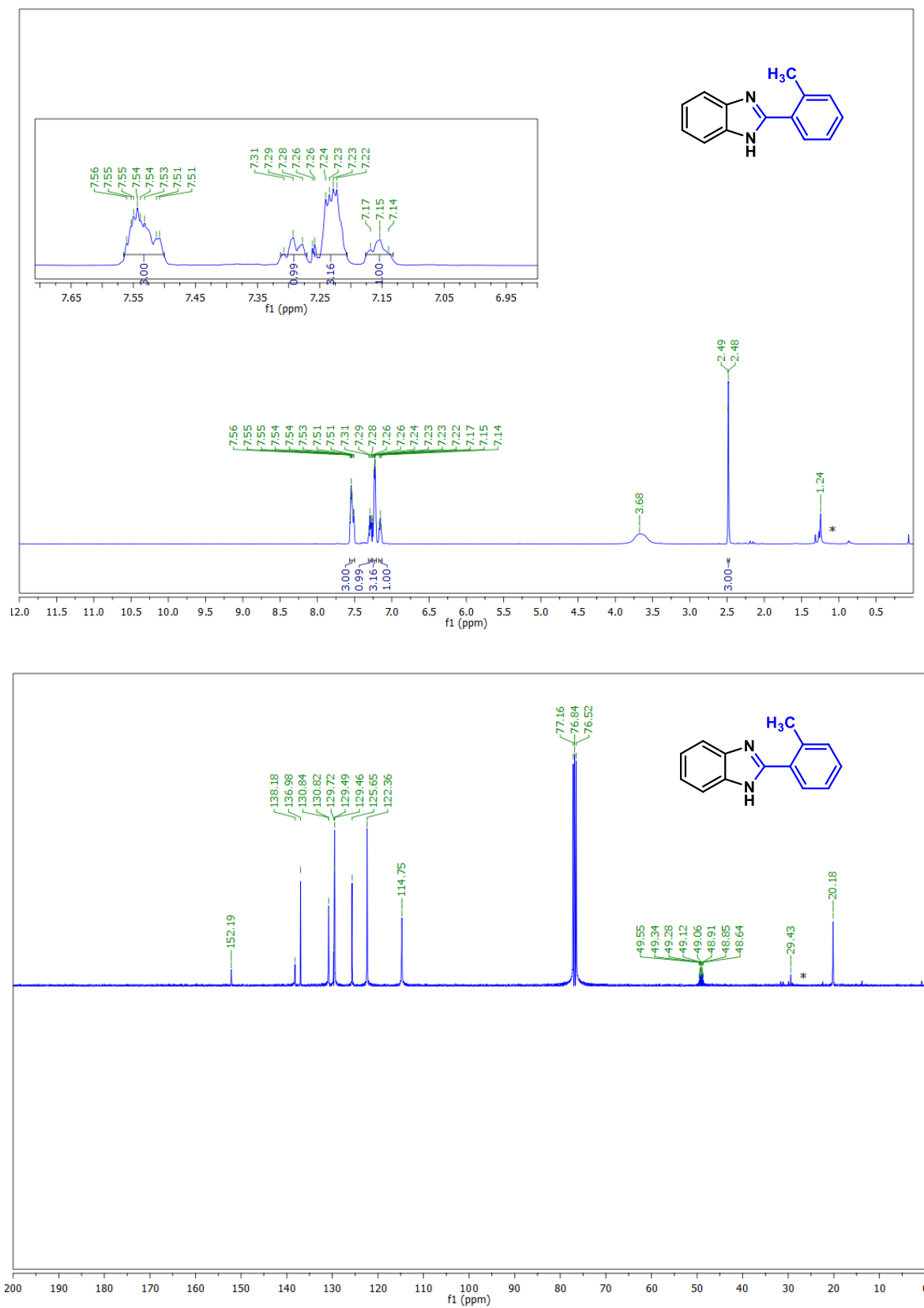
**Fig S2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5a** (in  $\text{DMSO-d}_6$  and  $\text{CDCl}_3$ + 1 drop  $\text{CD}_3\text{OD}$  solvent) ( $^x$ water, \*hexane,  $^+$ ethyl acetate).



**Fig S3.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5b** (in DMSO-d<sub>6</sub> solvent) (x water, + ethyl acetate).

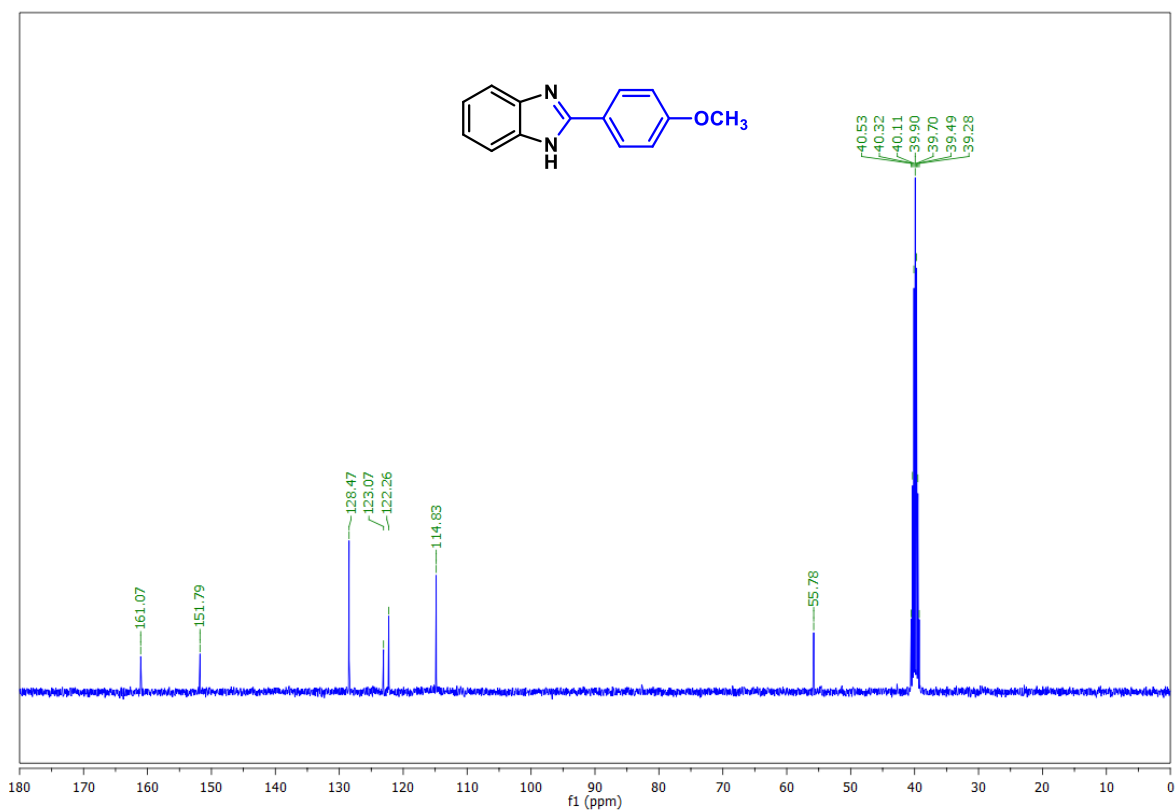
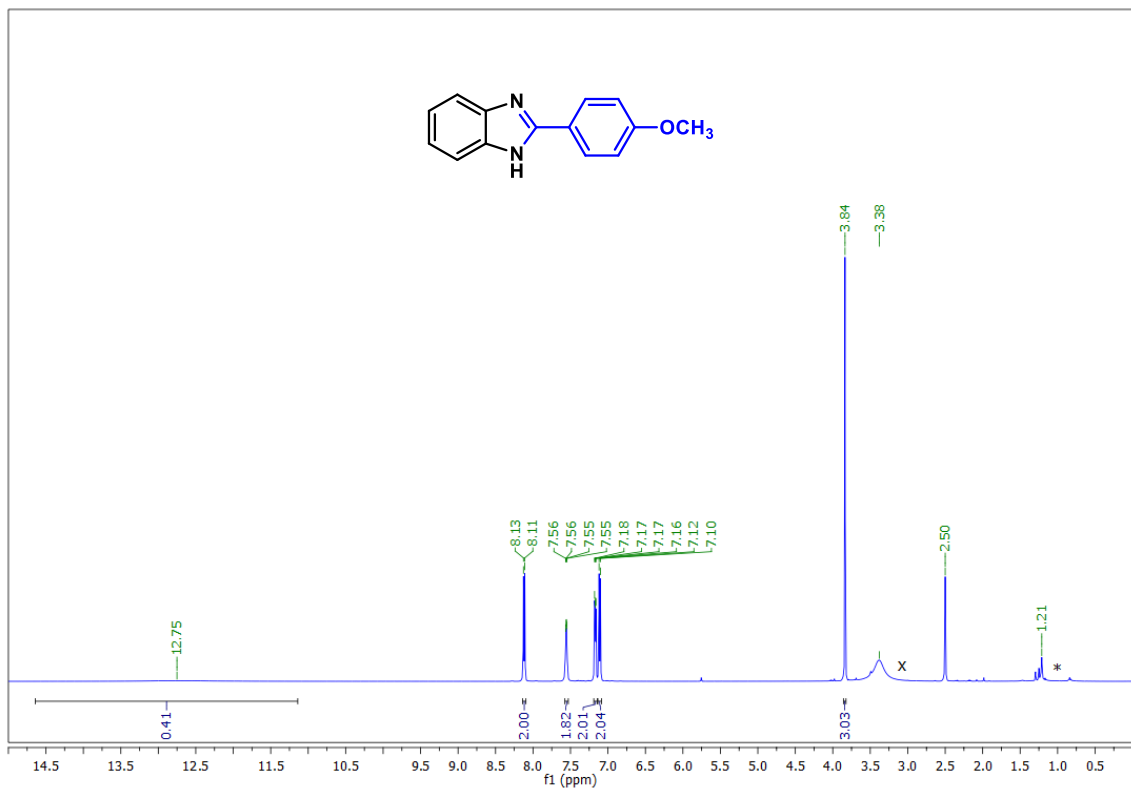


**Fig S4.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5c** (in  $\text{CDCl}_3$ + 1 drop  $\text{CD}_3\text{OD}$  solvent) (\*hexane).

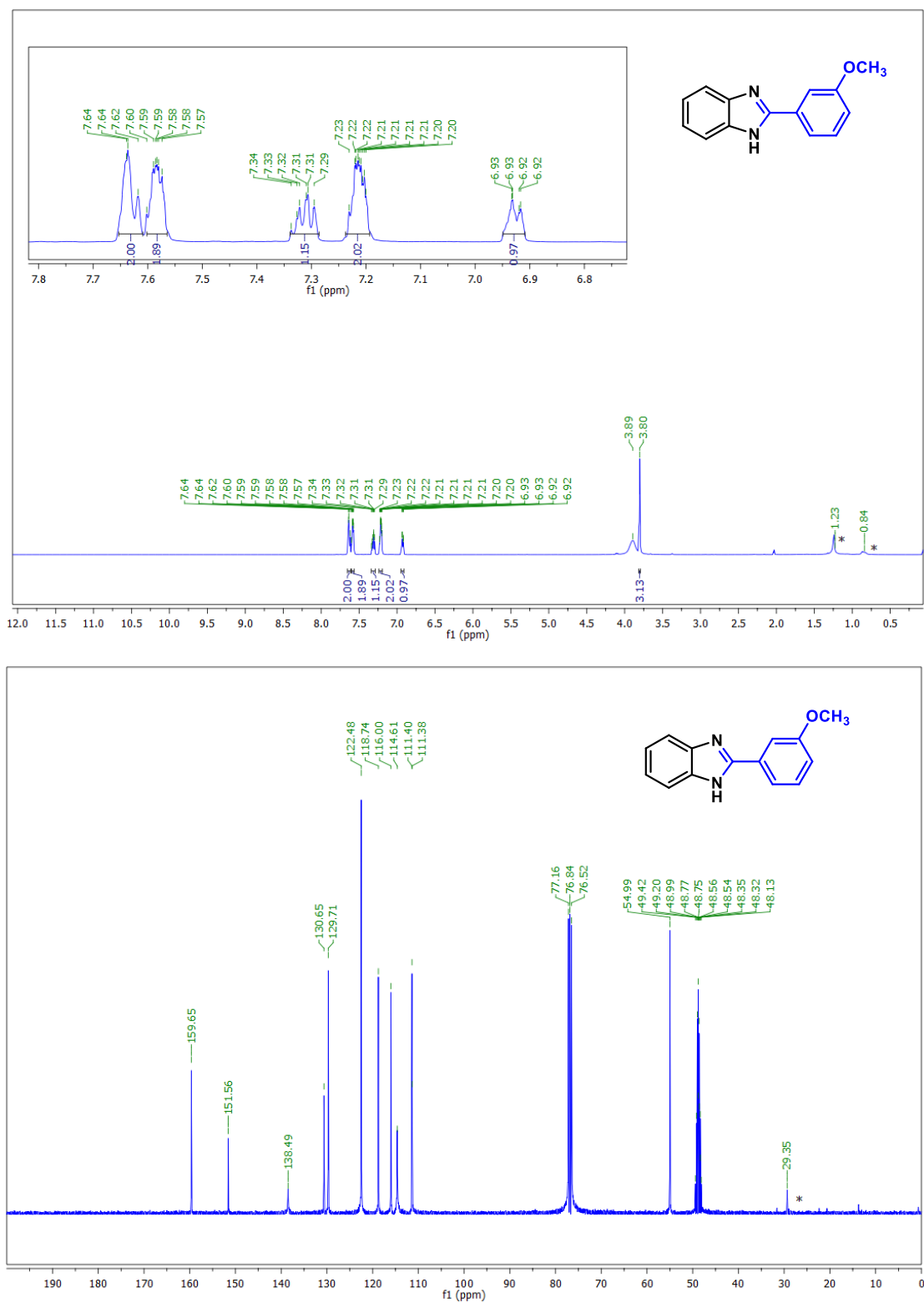


**Fig S5.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5d** (in CDCl<sub>3</sub>+ 1 drop CD<sub>3</sub>OD solvent) (\*hexane).

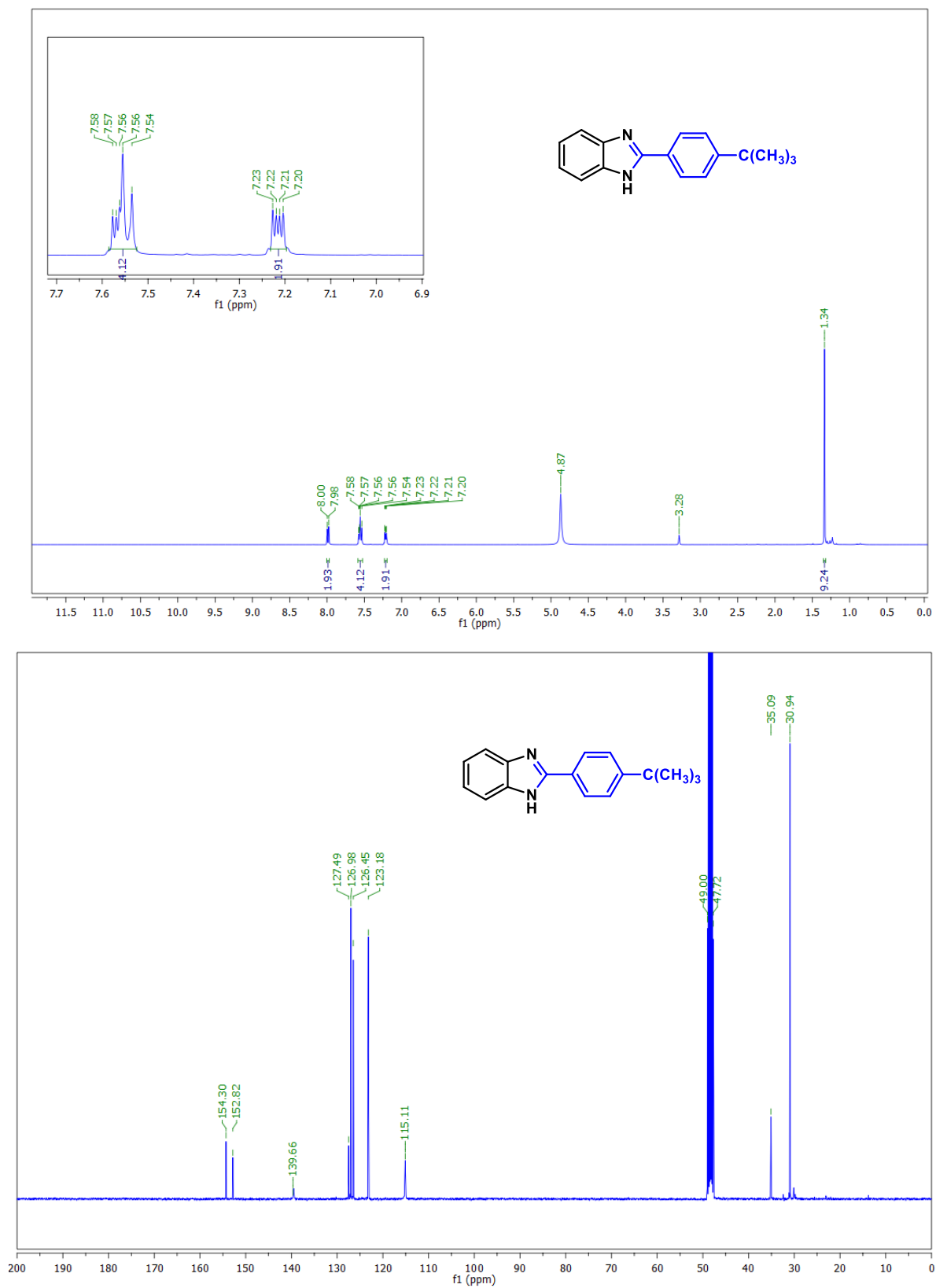




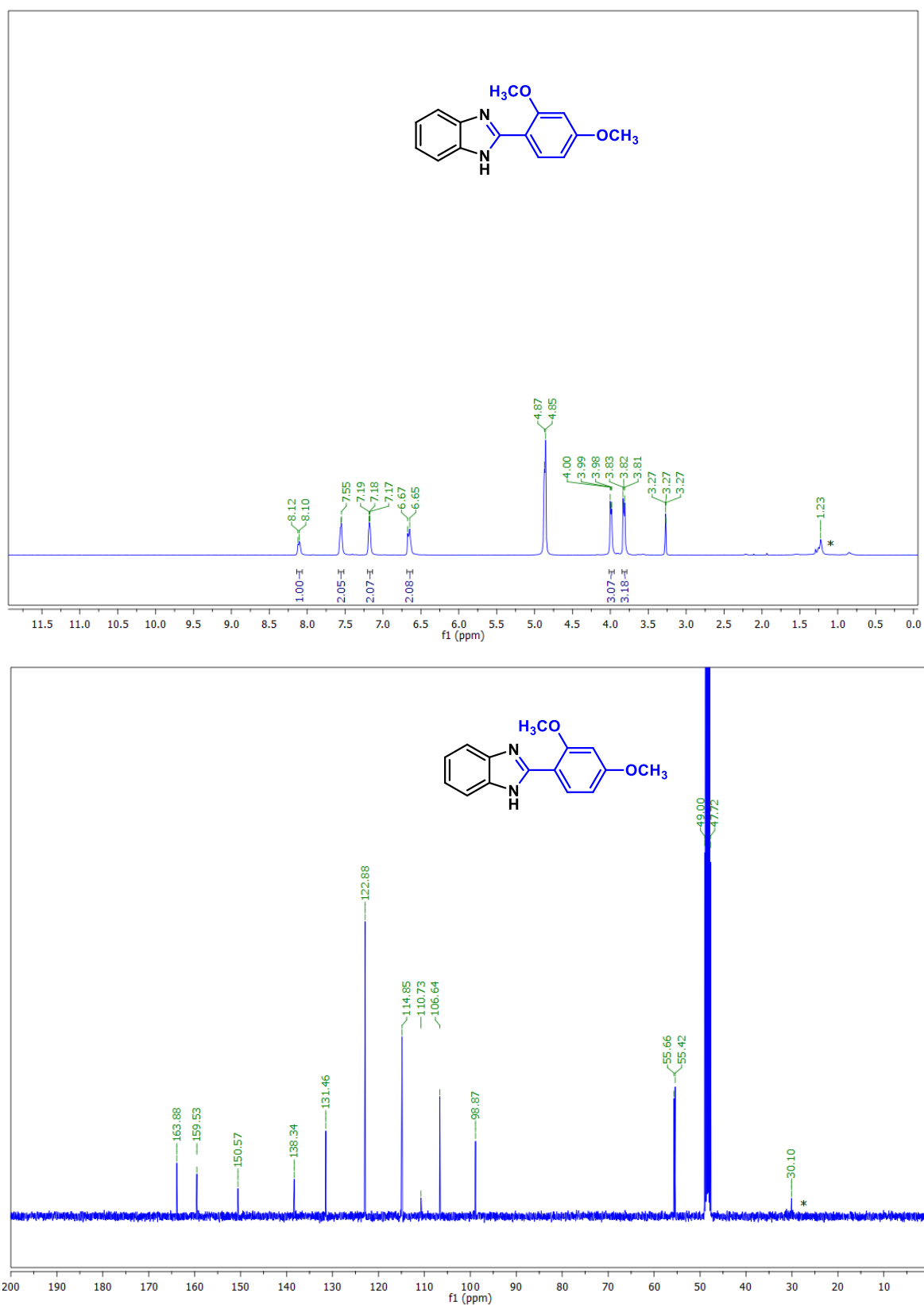
**Fig S6.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5e** (in DMSO-d<sub>6</sub> solvent) (\*water,\*hexane).



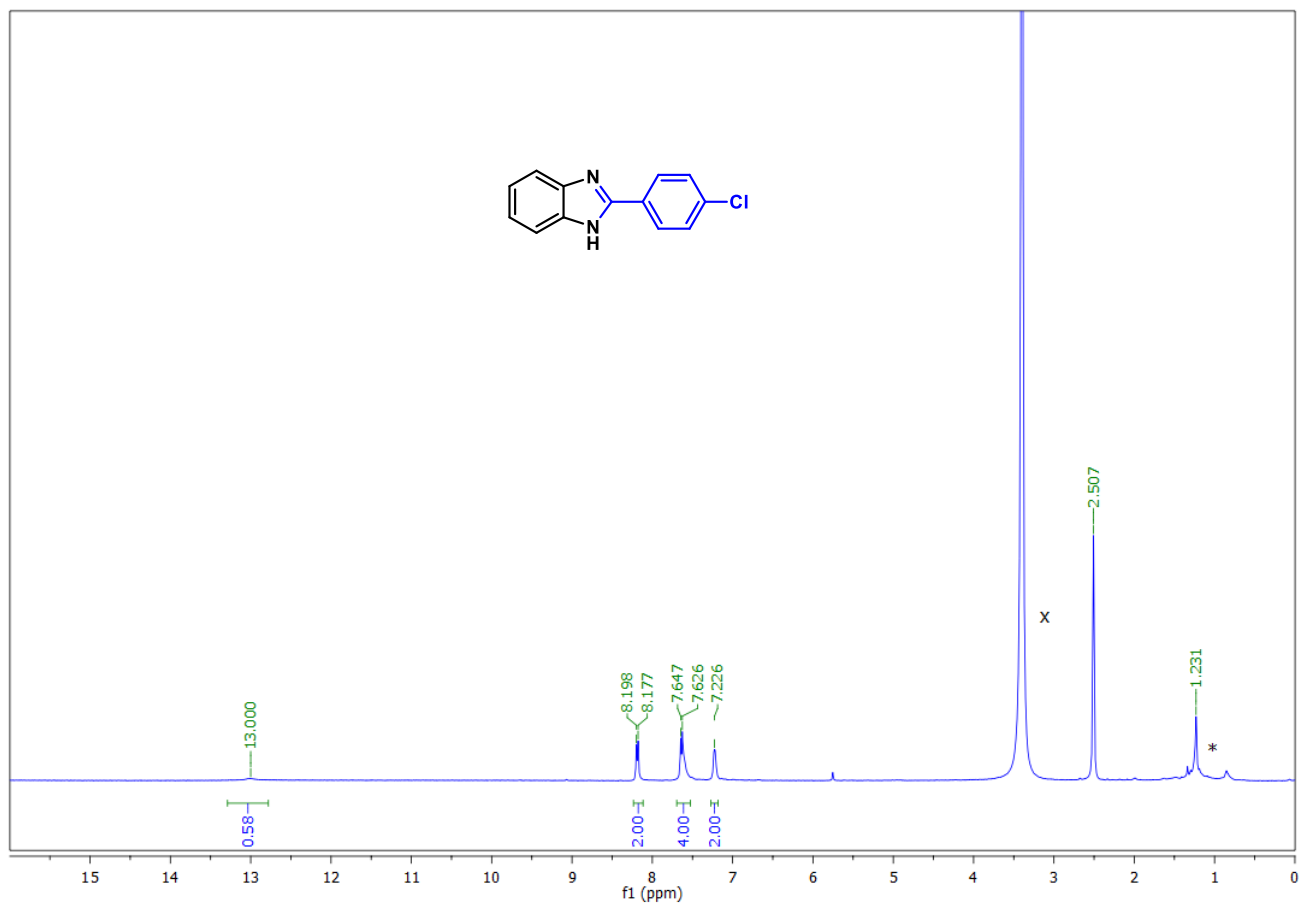
**Fig S7.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5f** (in CDCl<sub>3</sub>+ 1 drop CD<sub>3</sub>OD solvent) (\*hexane).



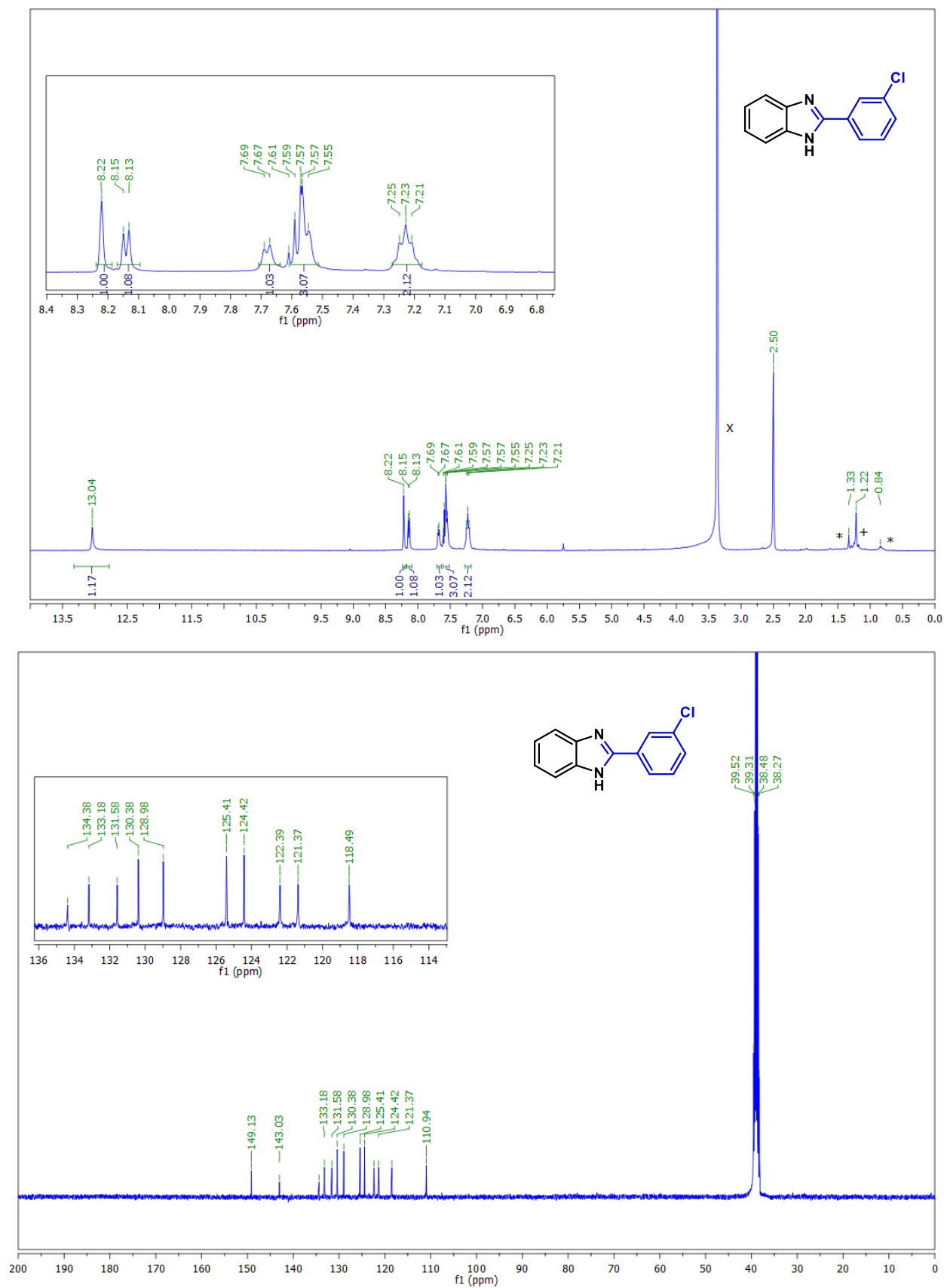
**Fig S8.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5g** (in  $\text{CD}_3\text{OD}$  solvent).



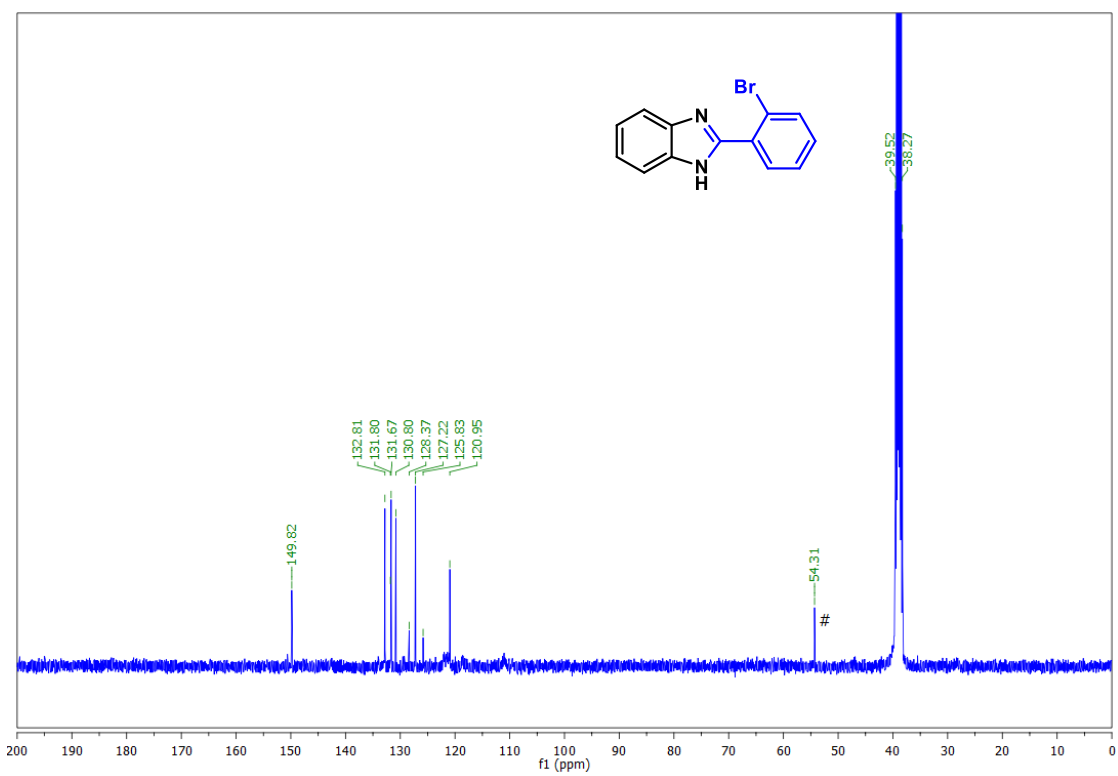
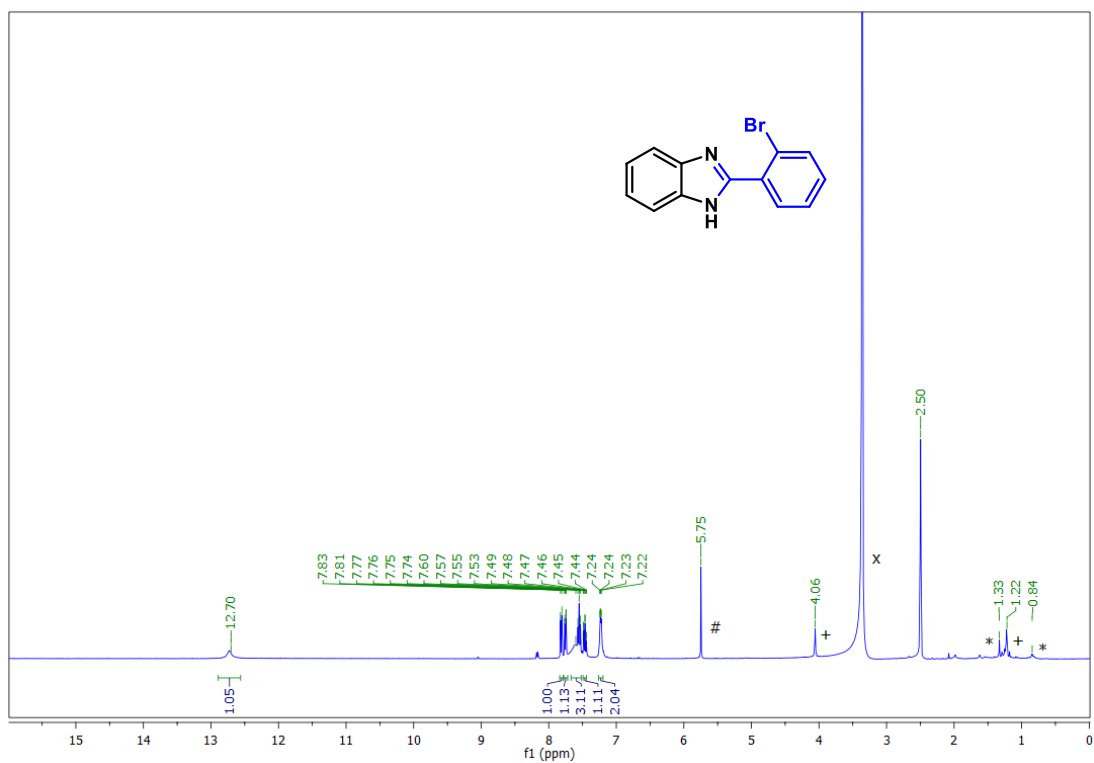
**Fig S9.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5h** (in CD<sub>3</sub>OD solvent) (\*hexane).



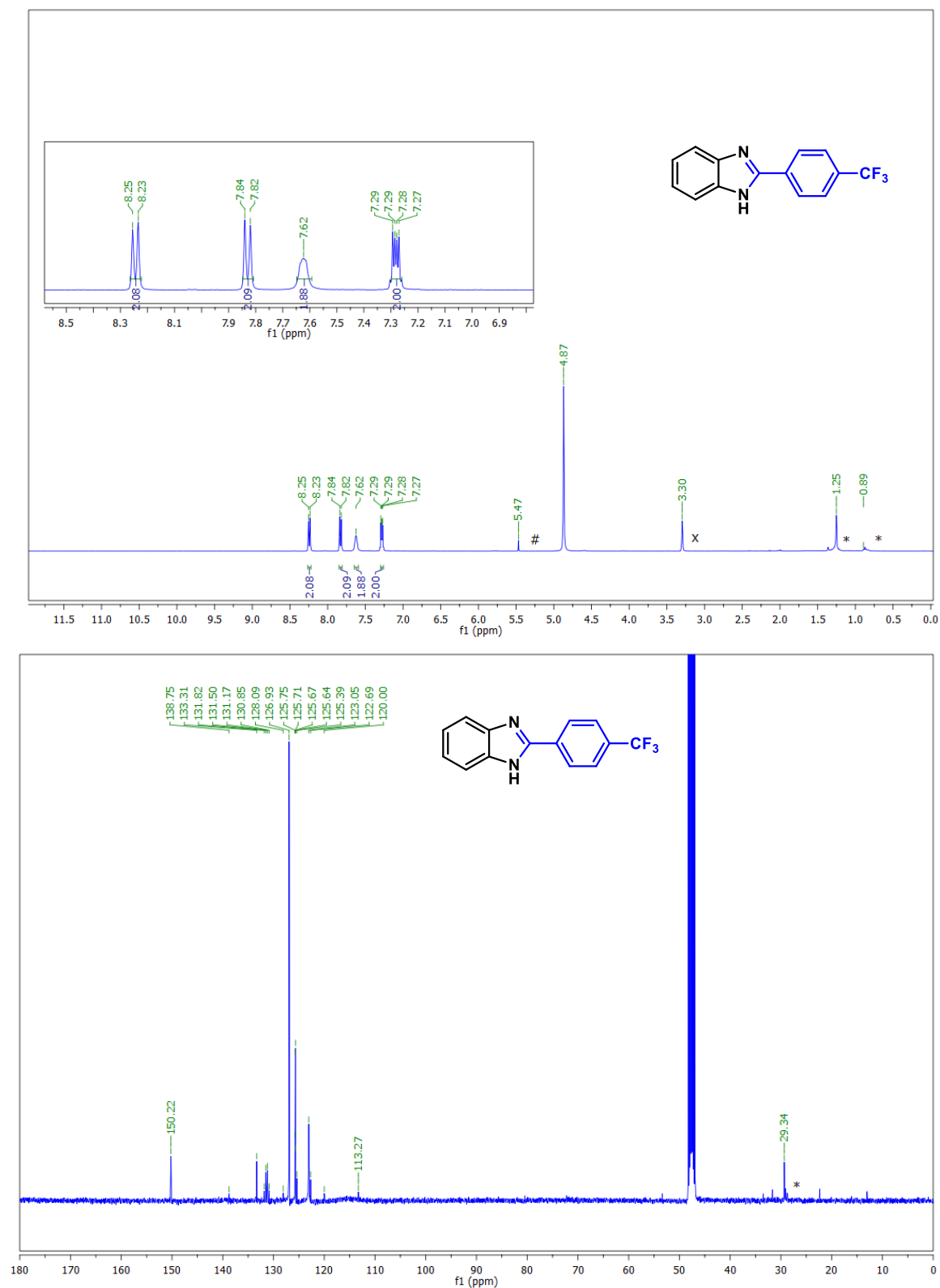
**Fig S10.** <sup>1</sup>H spectrum of **5i** (in DMSO-d<sub>6</sub> solvent) (xwater,\*hexane).



**Fig S11.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5j** (in DMSO-d<sub>6</sub> solvent) (Xwater, \*hexane, +ethyl acetate).

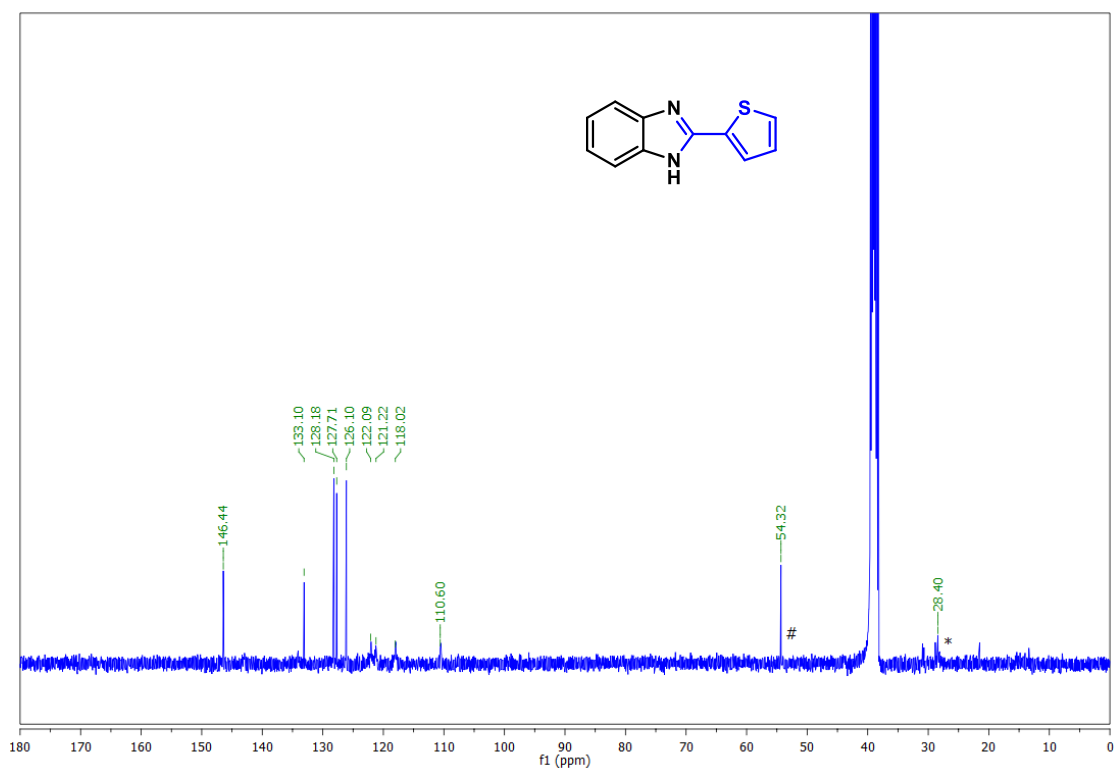
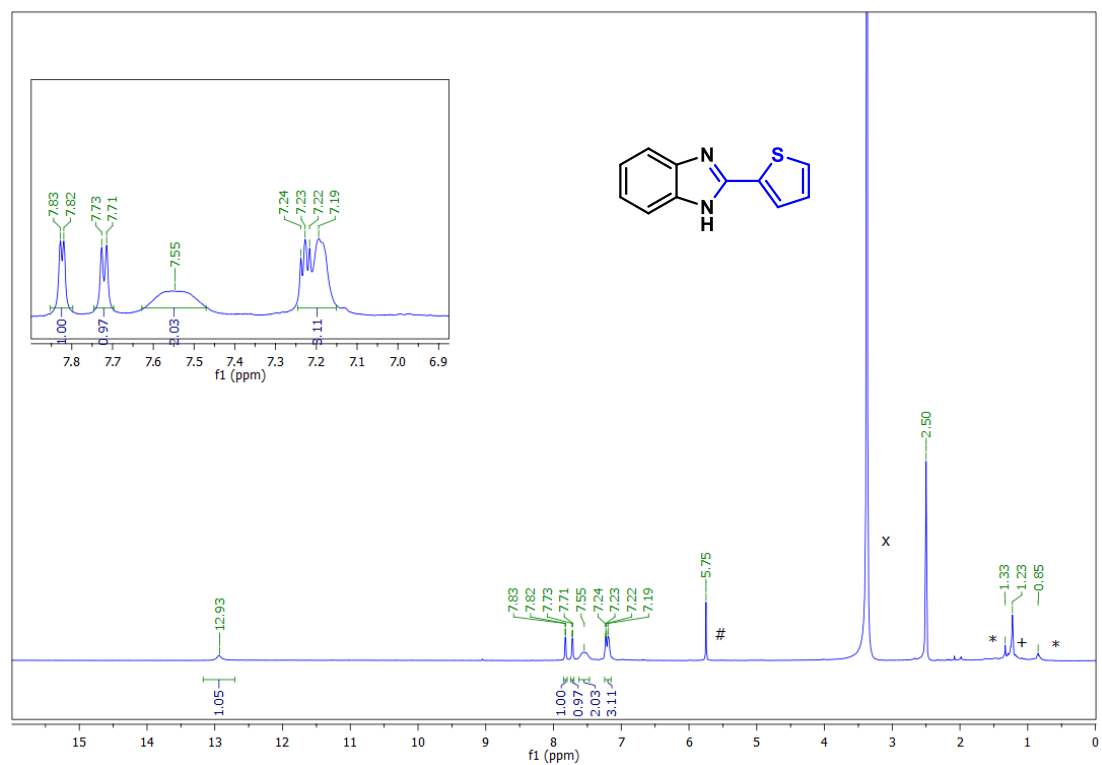


**Fig S12.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5k** (in DMSO-d<sub>6</sub> solvent) (#dichloromethane, +ethyl acetate, xwater, \*hexane).

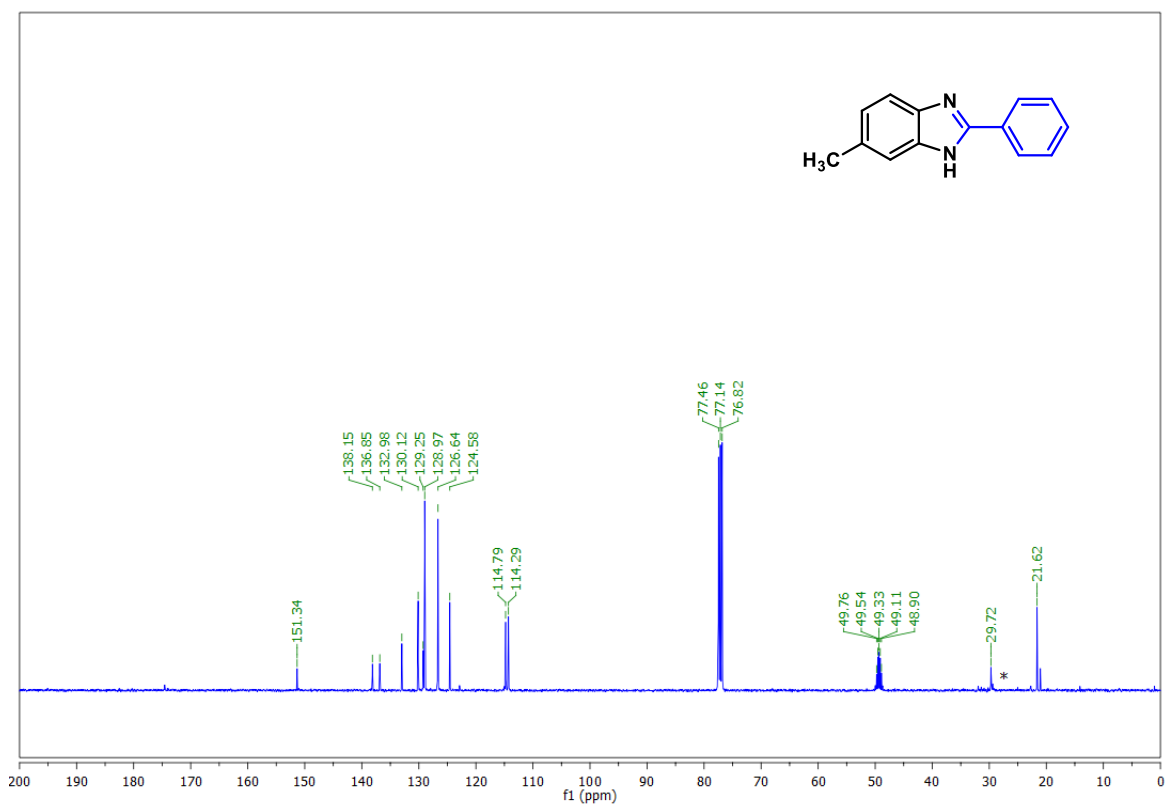
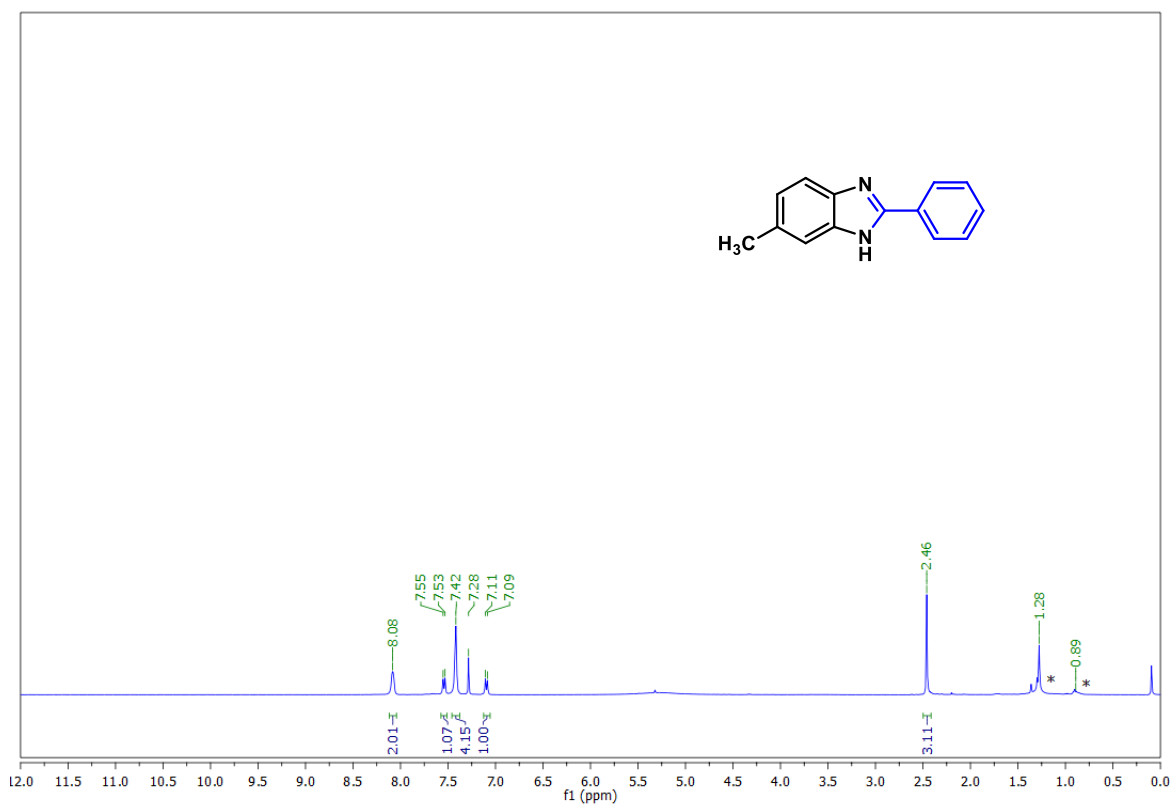


**Fig S13.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **51** (in  $\text{CD}_3\text{OD}$  solvent) (#dichloromethane,  $^x$ water,  $^*$ hexane).

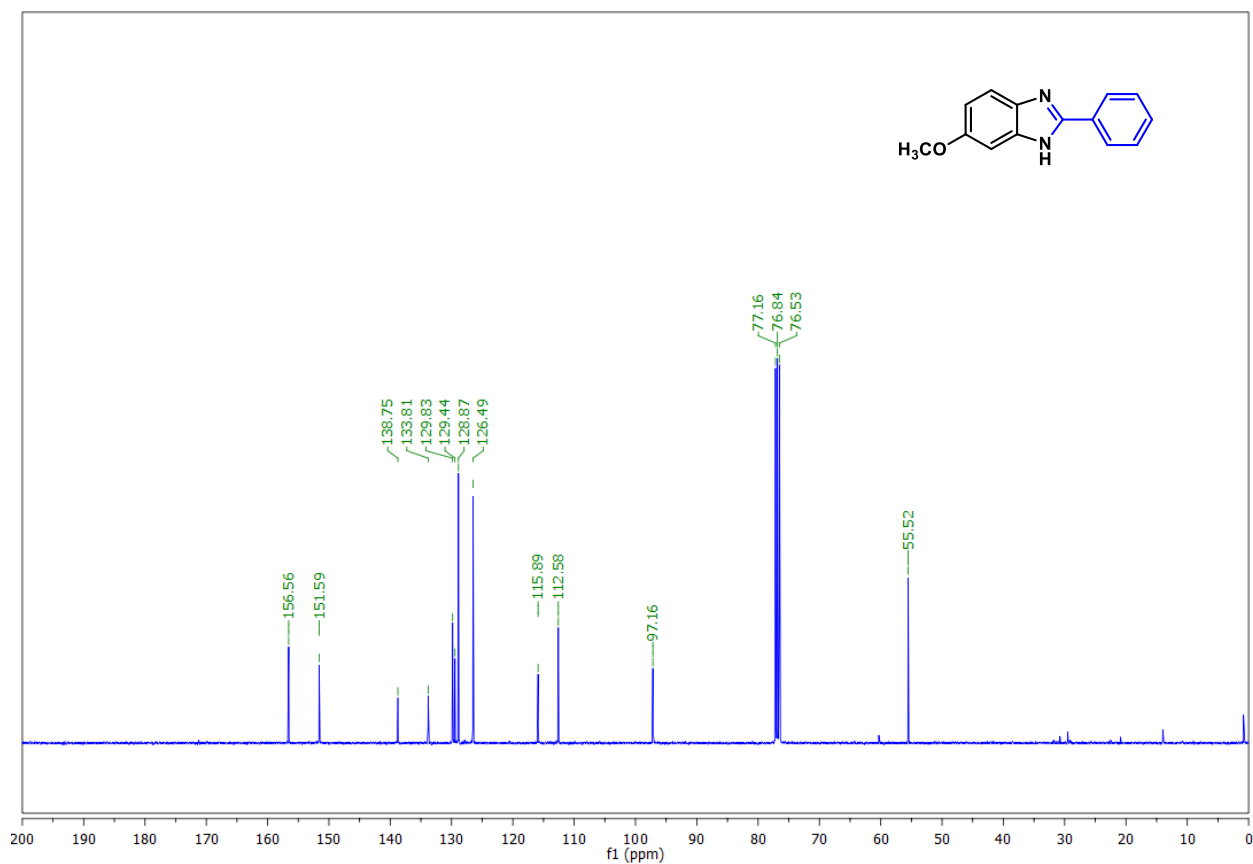
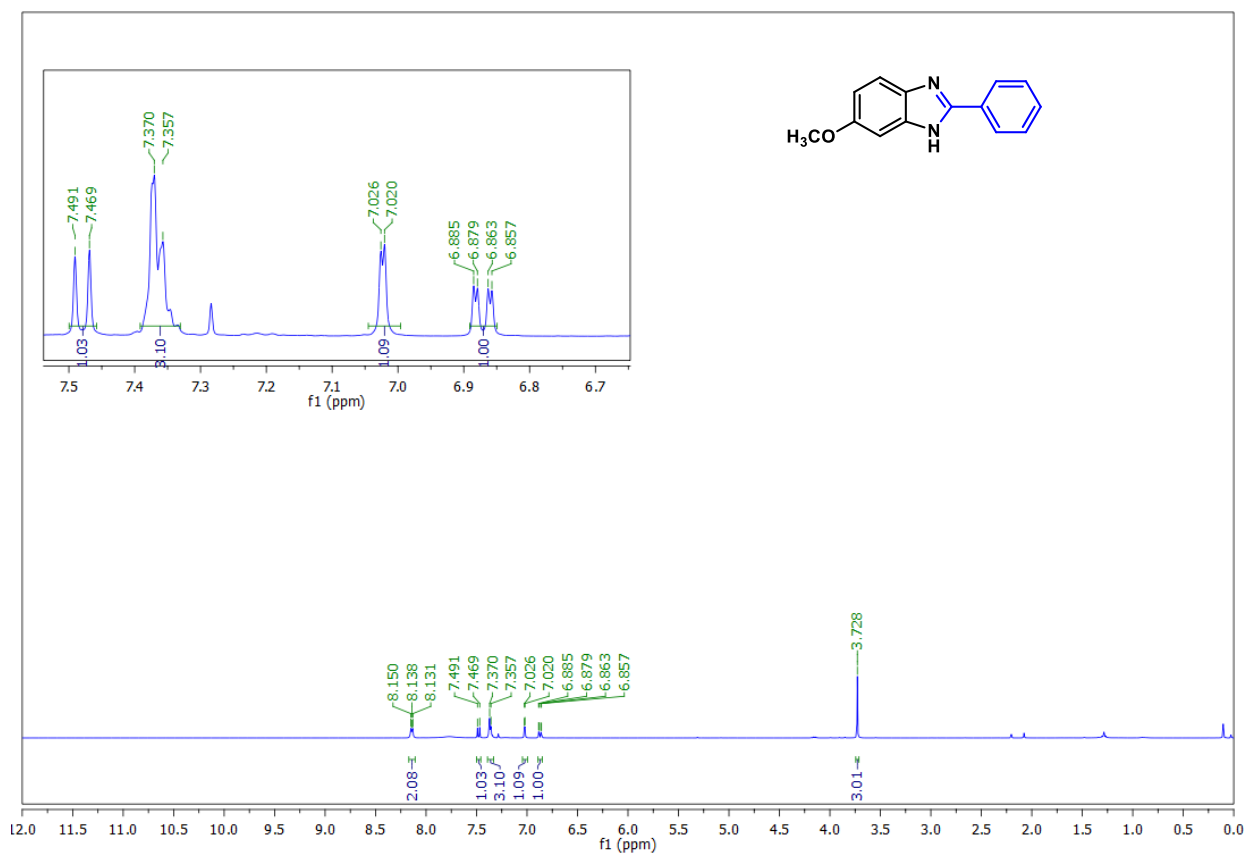




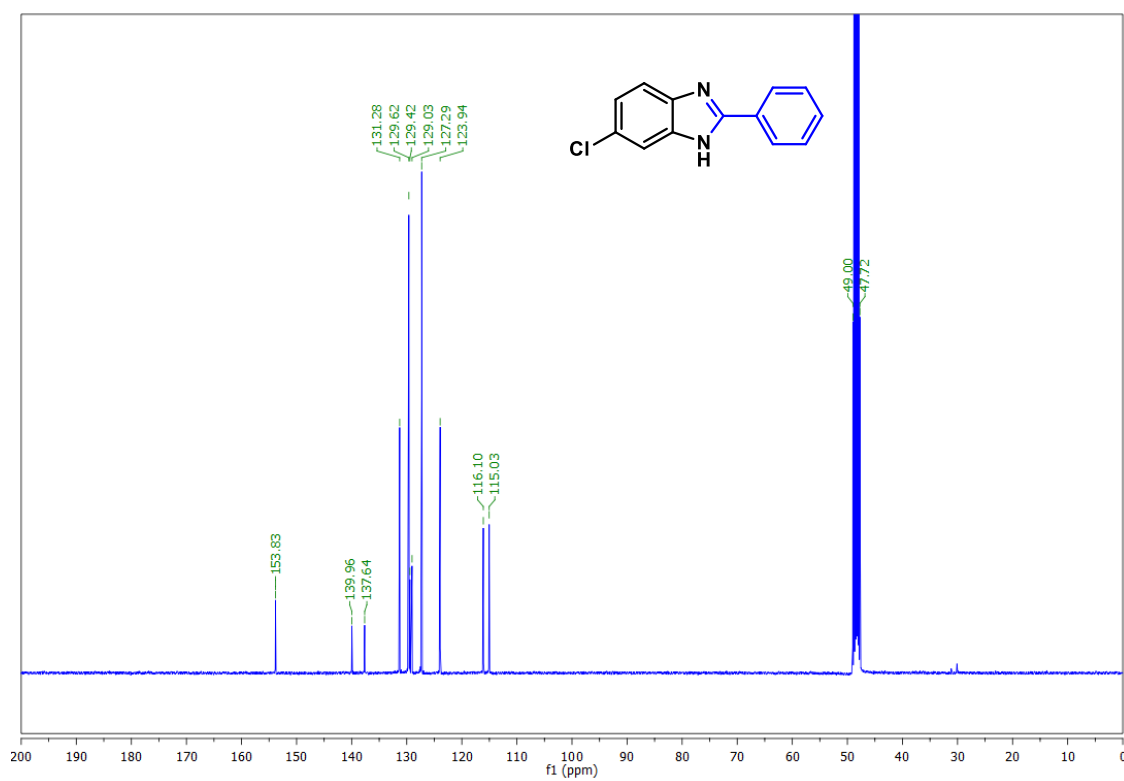
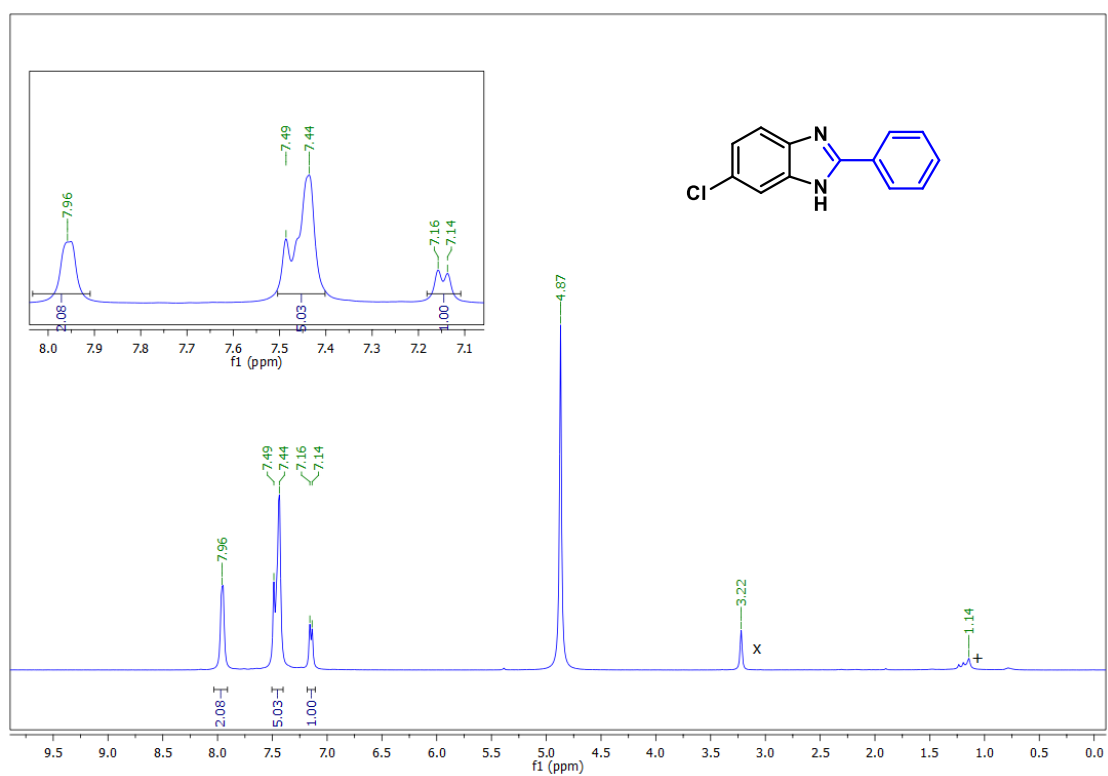
**Fig S14.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5m** (in DMSO-d<sub>6</sub> solvent) (# dichloromethane, + ethyl acetate, <sup>x</sup>water, \*hexane).



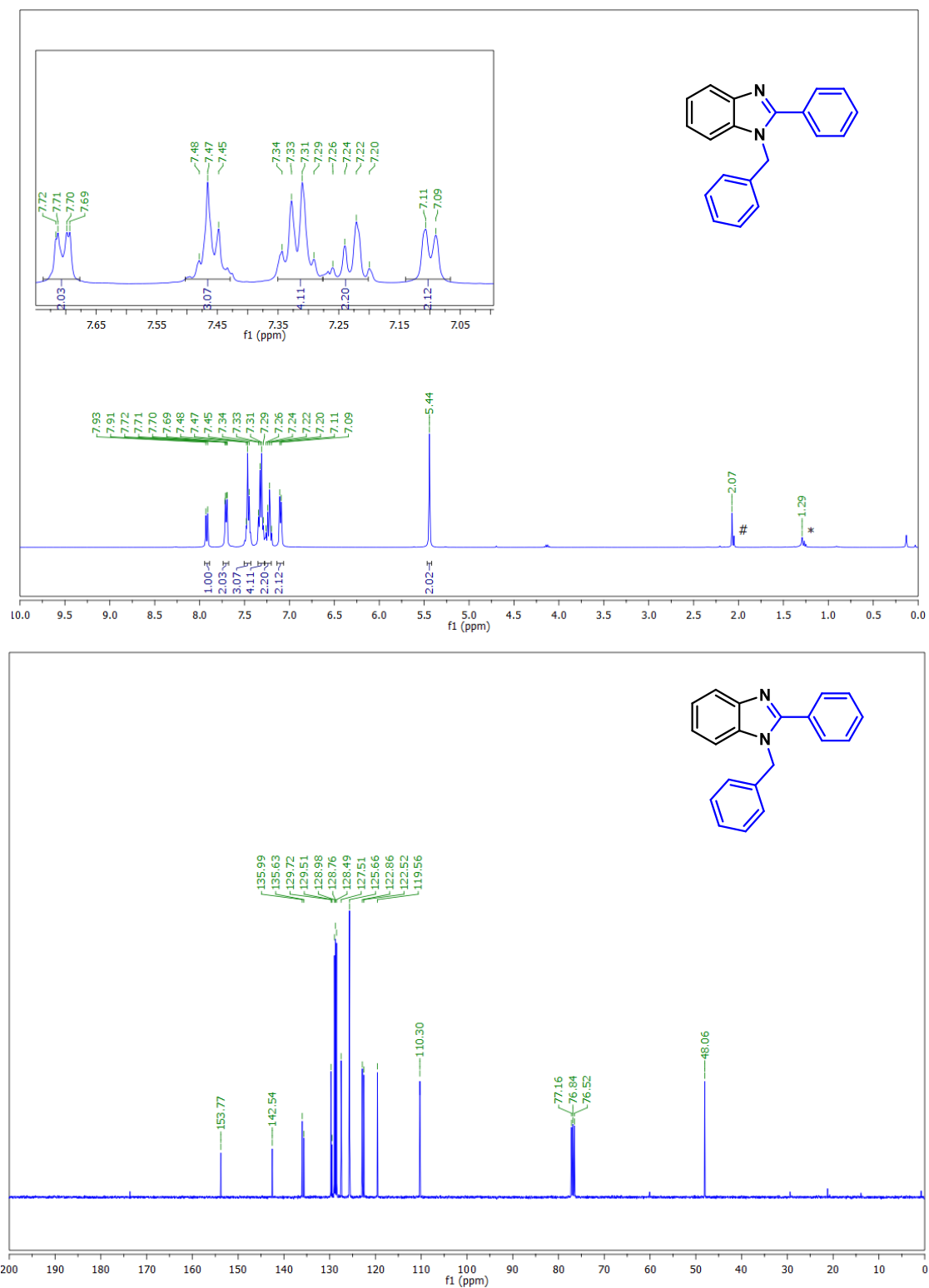
**Fig S15.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5n** (in CDCl<sub>3</sub> and CDCl<sub>3</sub>+1 drop CD<sub>3</sub>OD solvent) (\*hexane).



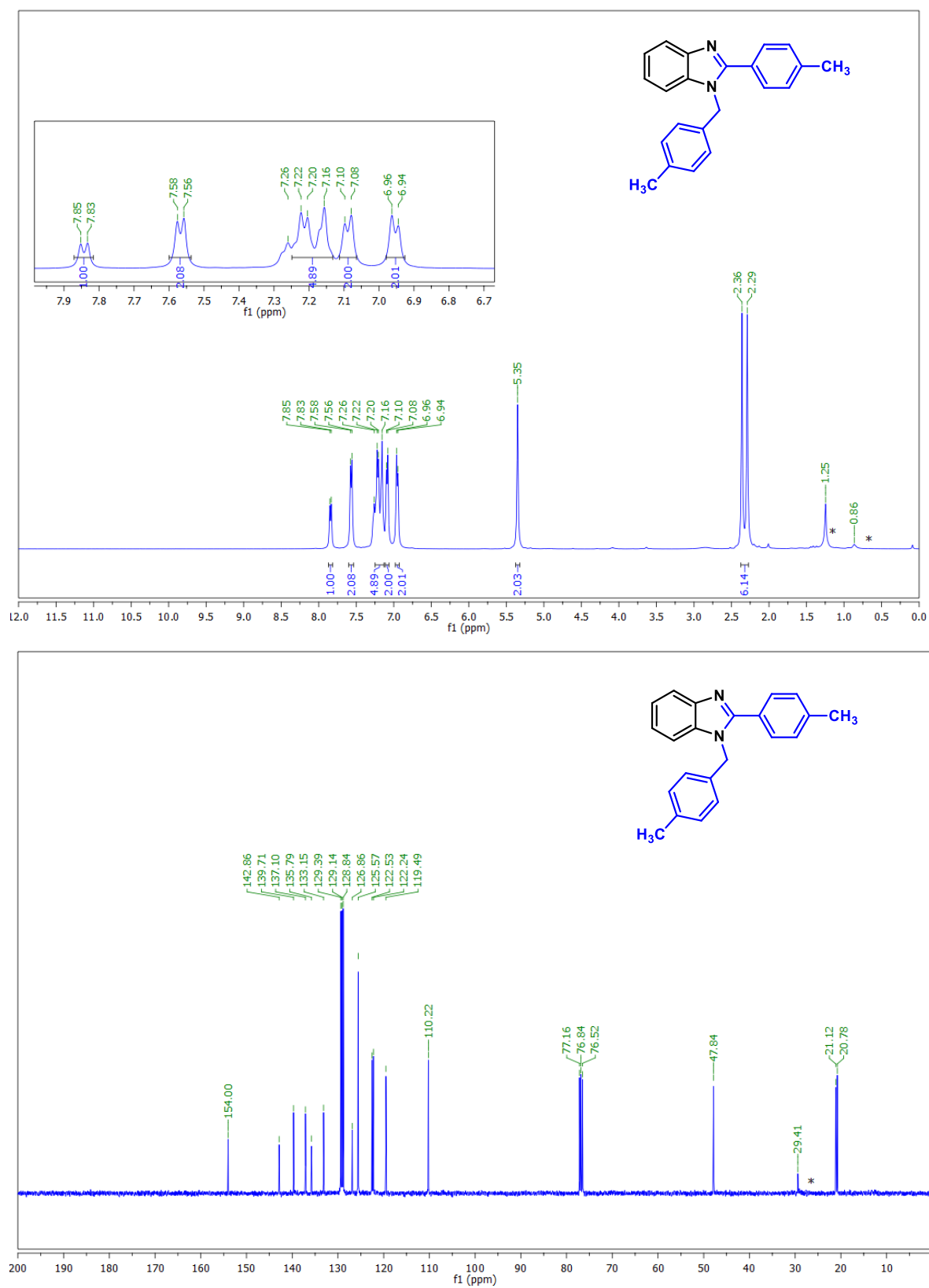
**Fig S16.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **5o** (in  $\text{CDCl}_3$  solvent).



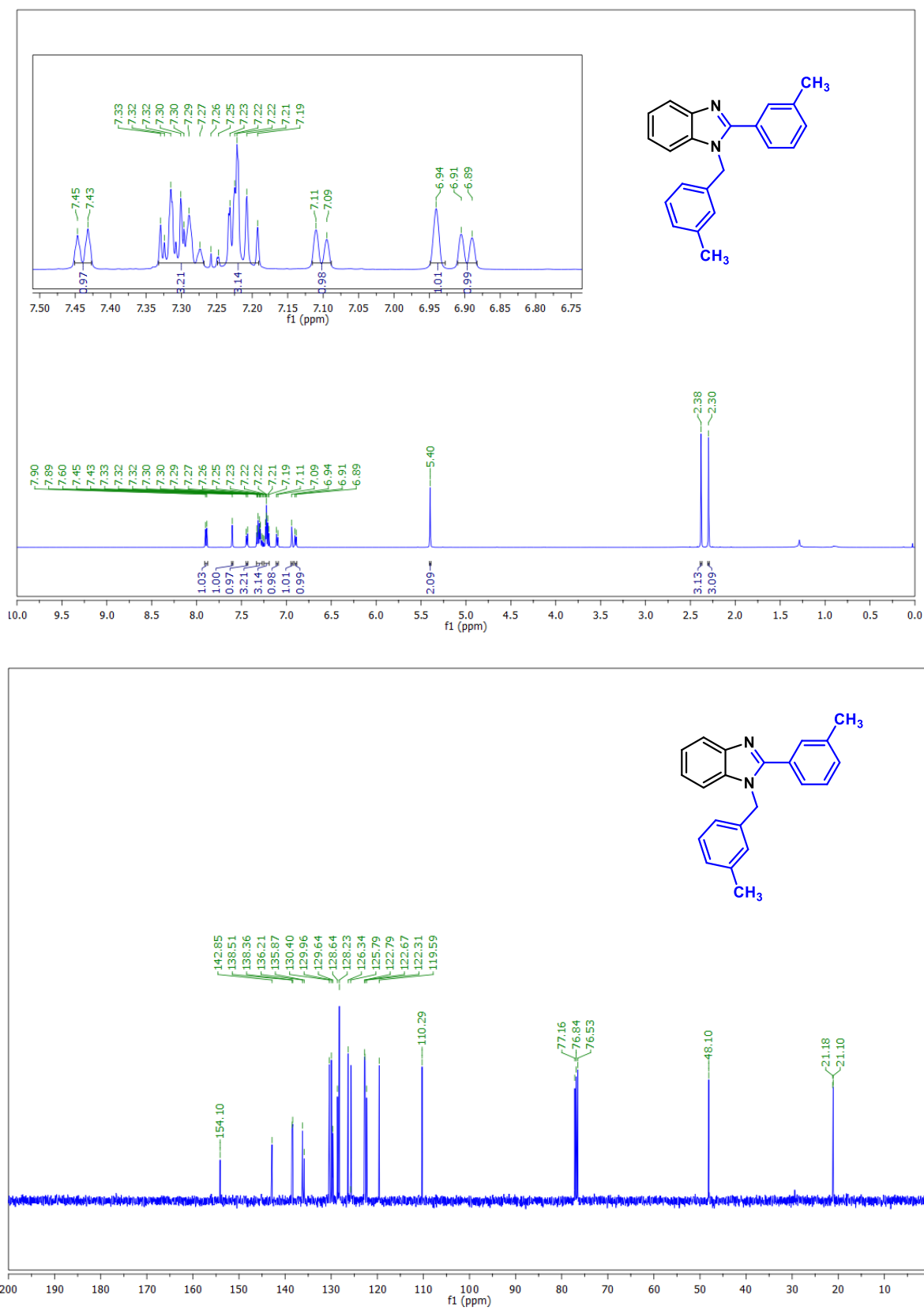
**Fig S17.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5p** (in CD<sub>3</sub>OD solvent) (+ethyl acetate, <sup>x</sup>water).



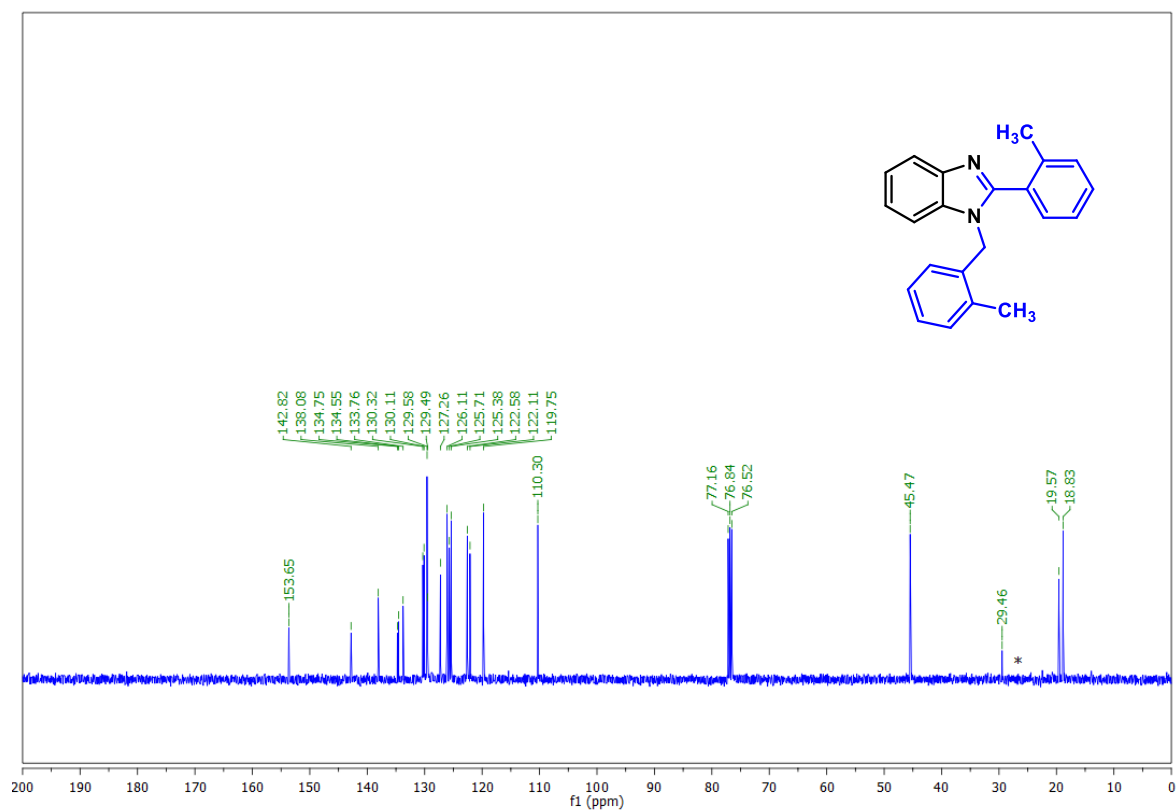
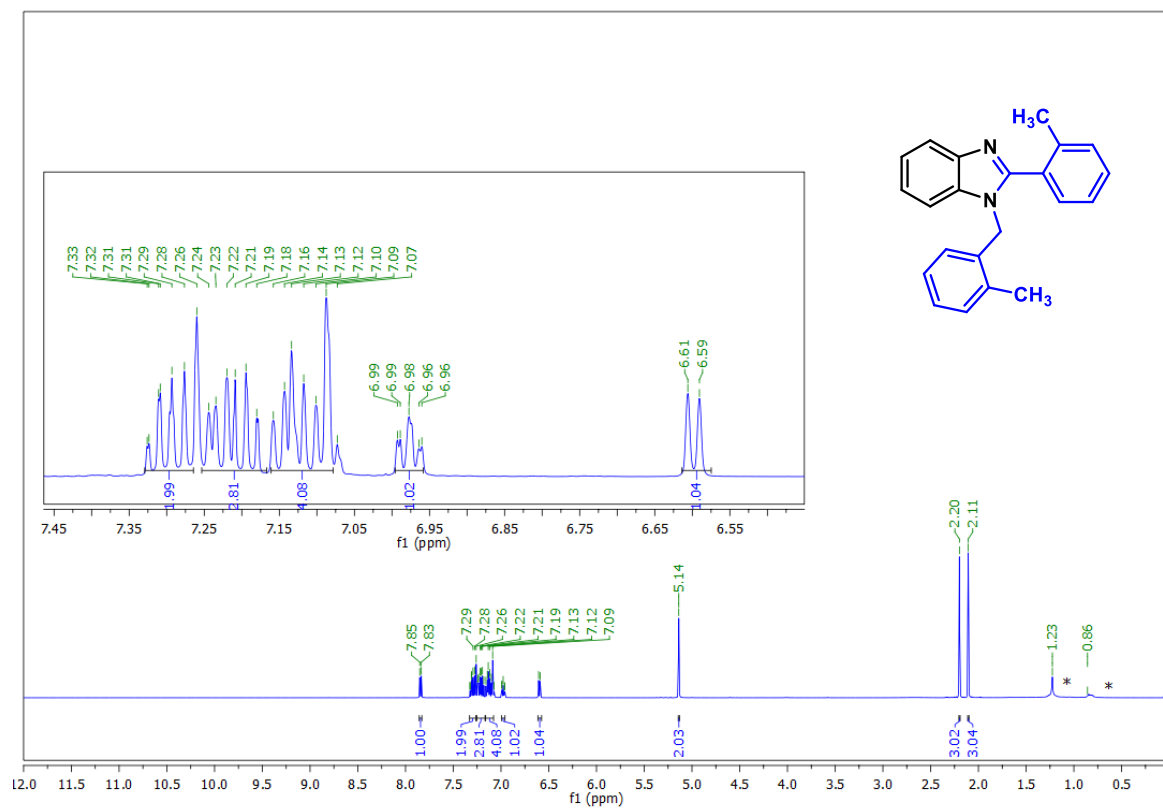
**Fig S18.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **6a** (in  $\text{CDCl}_3$  solvent) (#acetone, \*hexane).



**Fig S19.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6b** (in CDCl<sub>3</sub> solvent) (\*hexane).

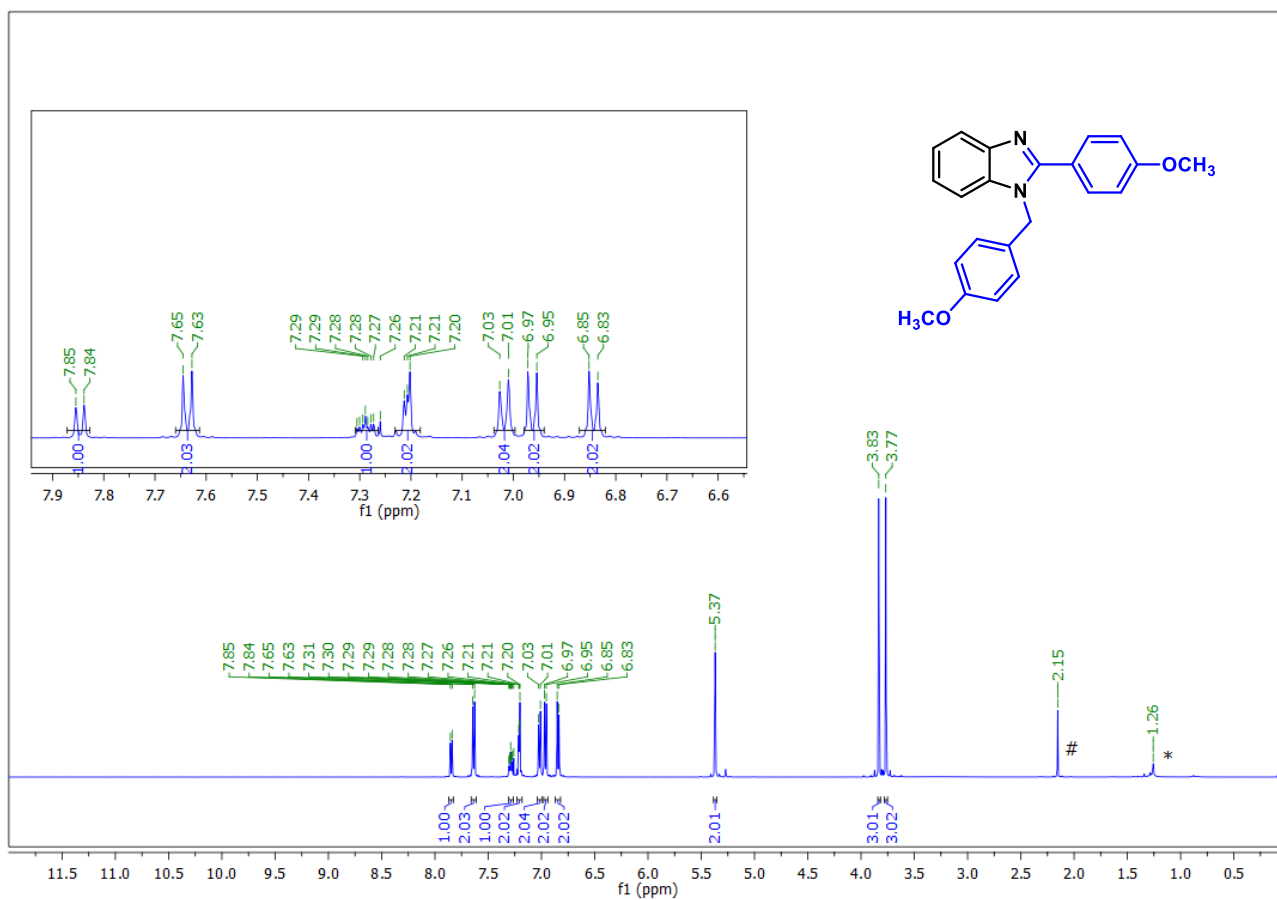


**Fig S20.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **6c** (in  $\text{CDCl}_3$  solvent).

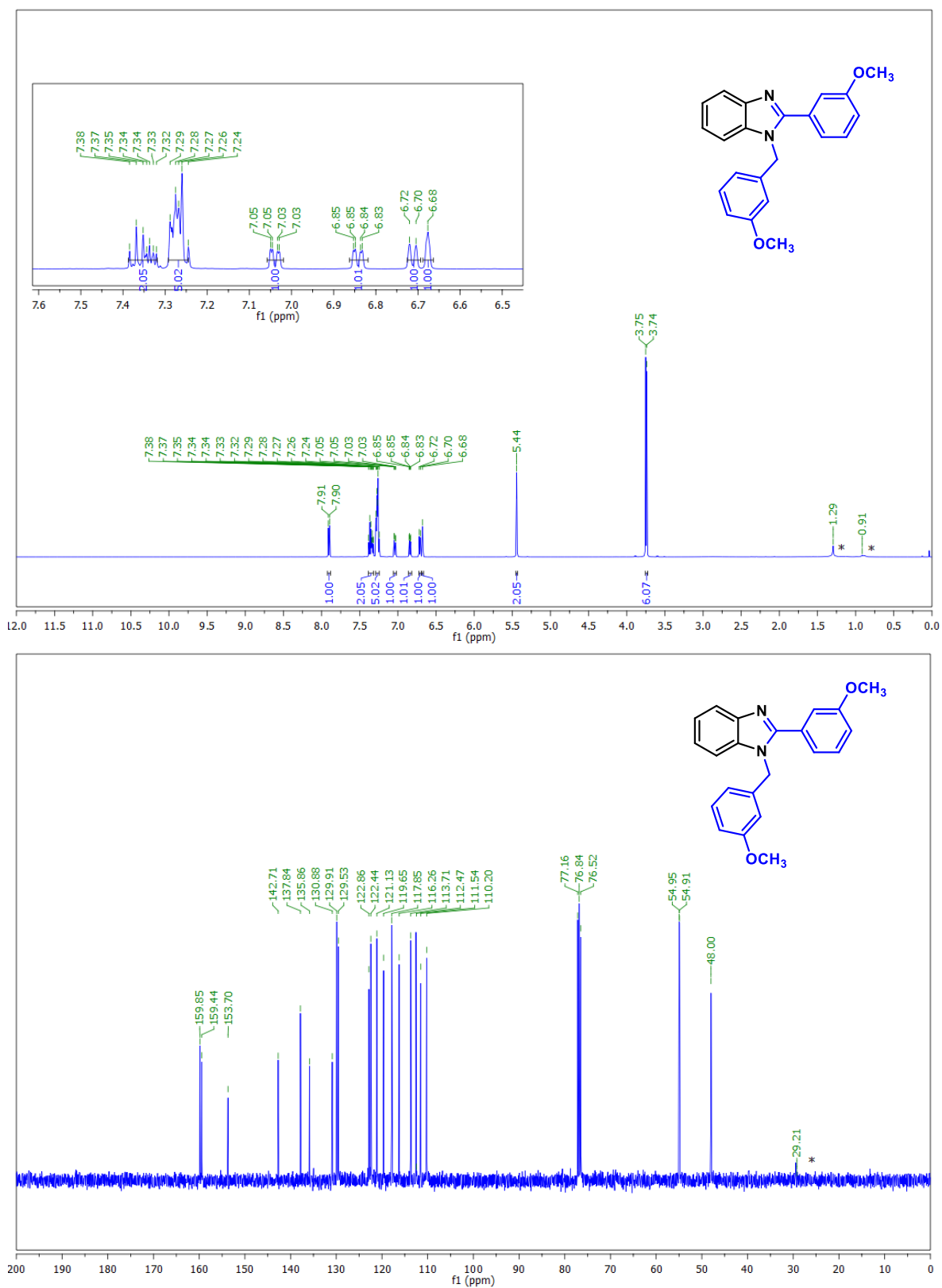


**Fig S21.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6d** (in CDCl<sub>3</sub> solvent) (\*hexane).

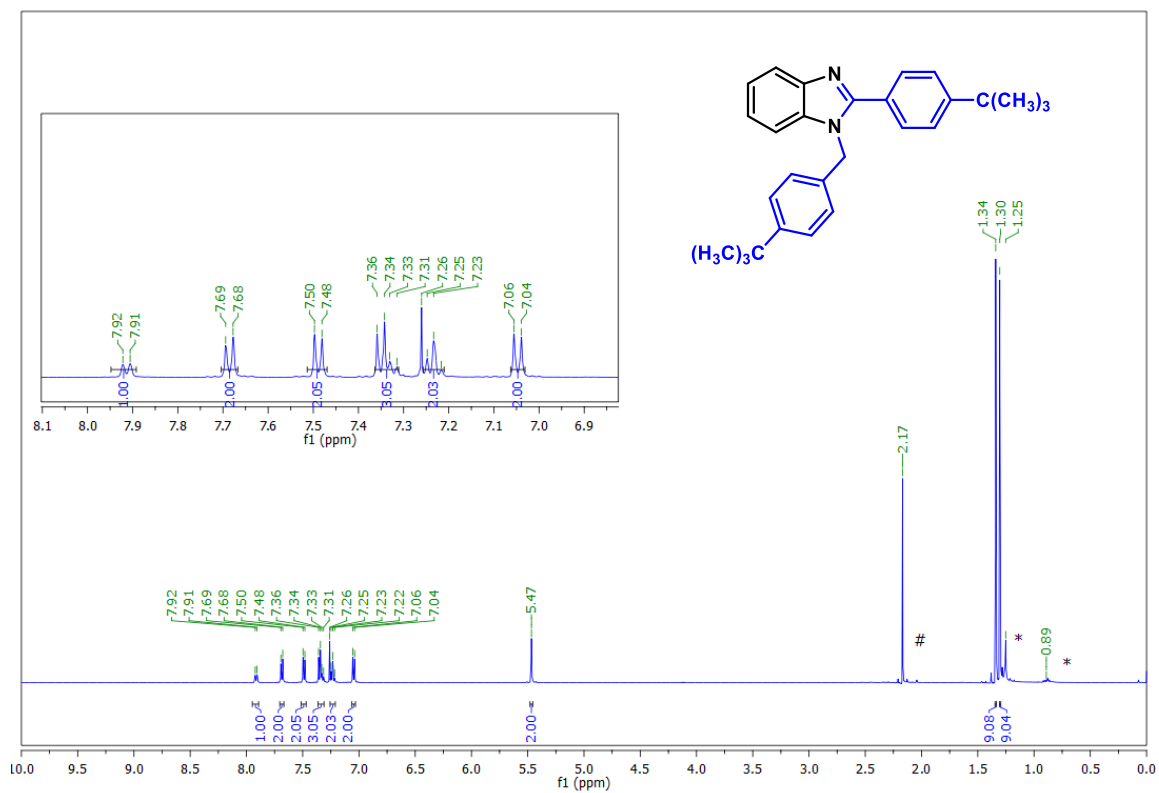




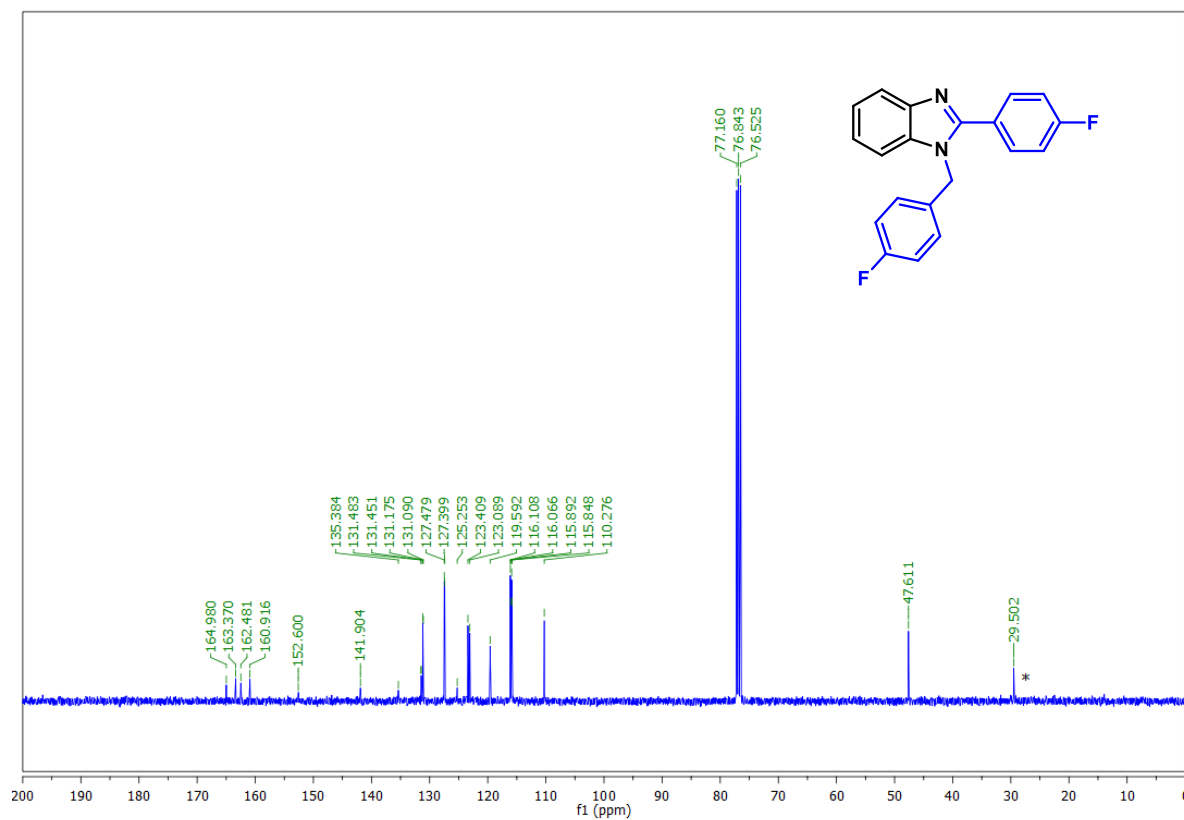
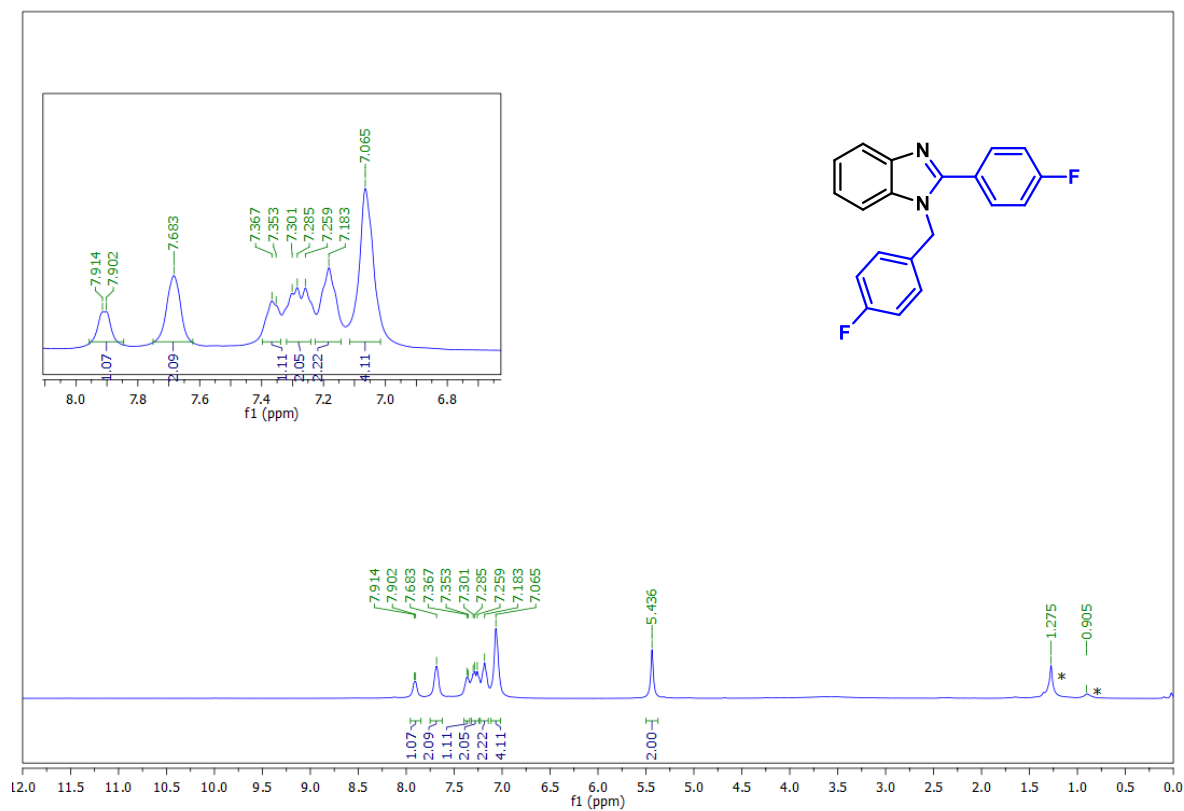
**Fig S22.** <sup>1</sup>H NMR spectrum of **6e** (in CDCl<sub>3</sub> solvent) (# acetone, \*hexane).



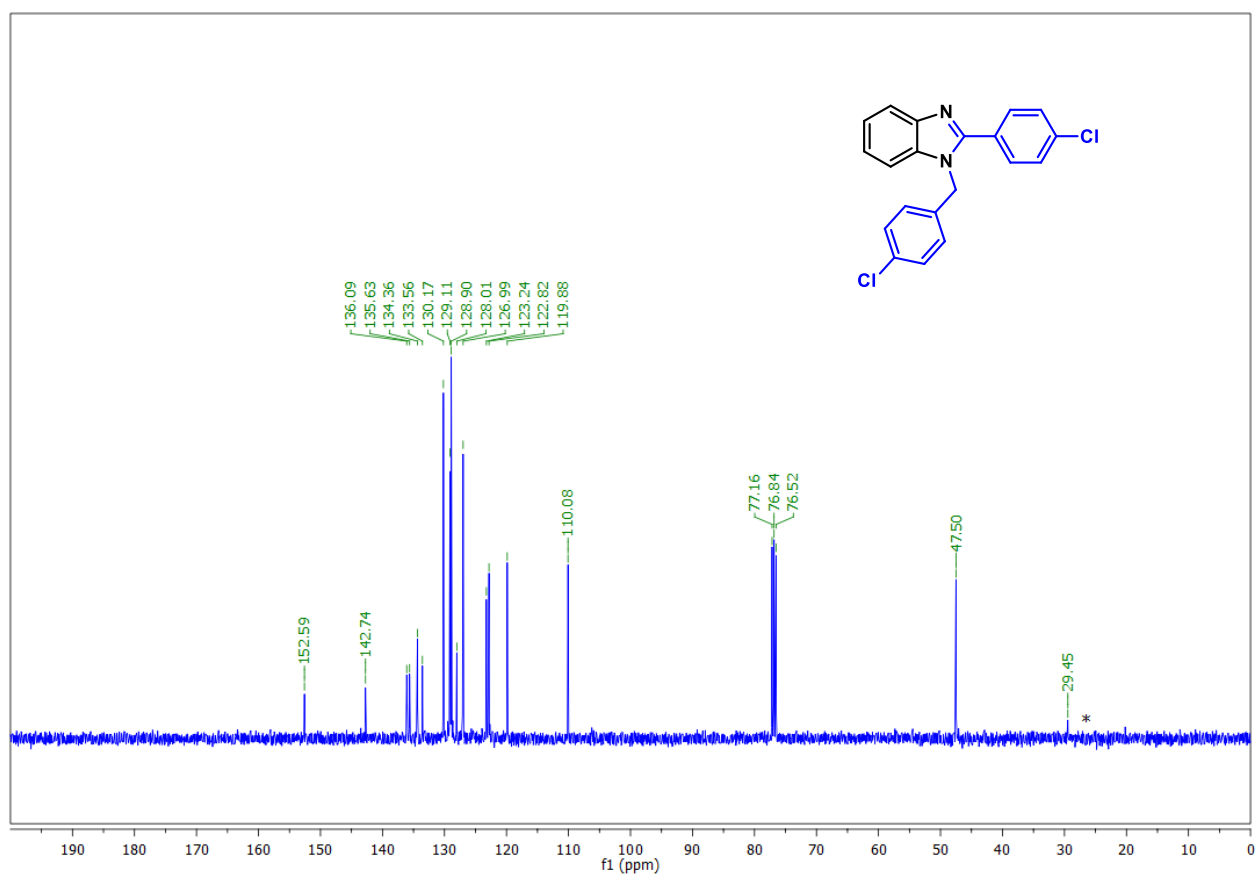
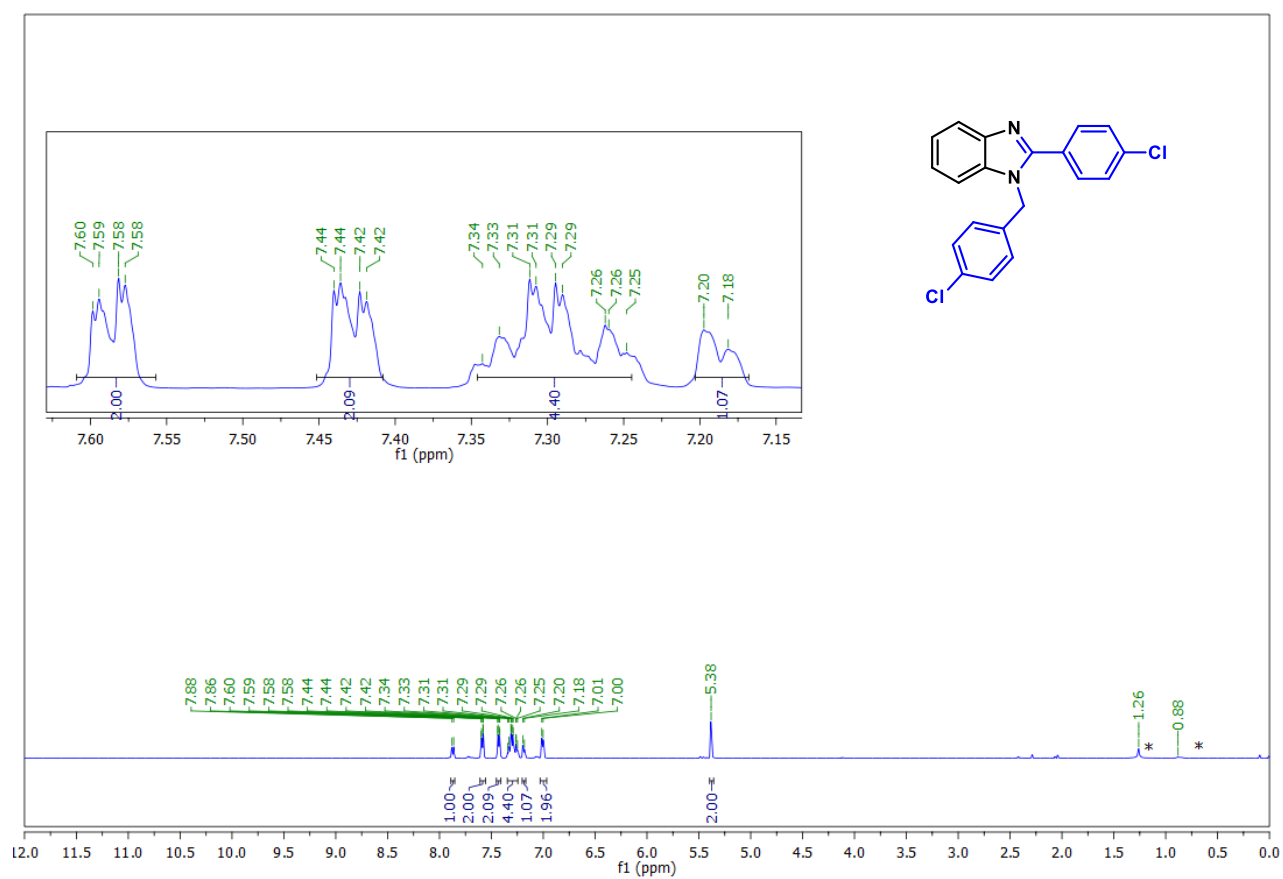
**Fig S23.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **6f** (in  $\text{CDCl}_3$  solvent) (\*hexane).



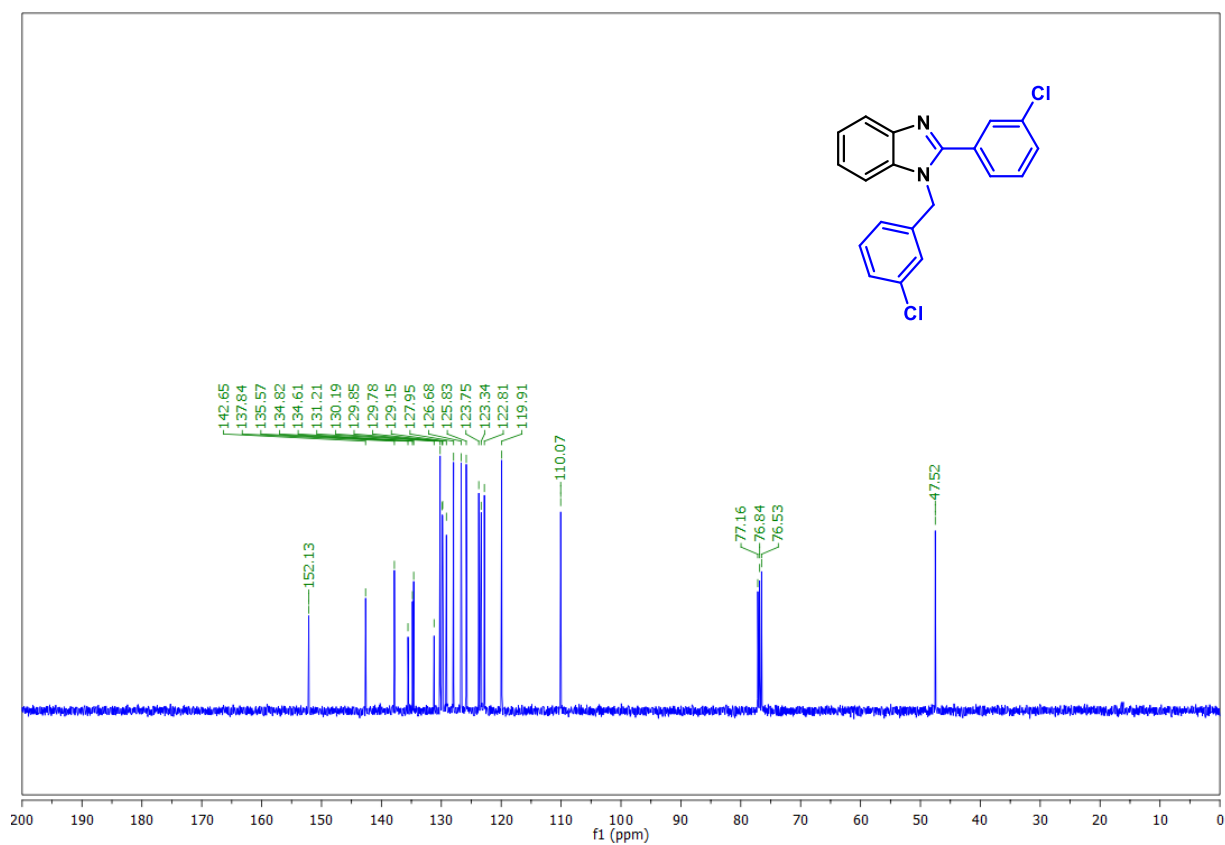
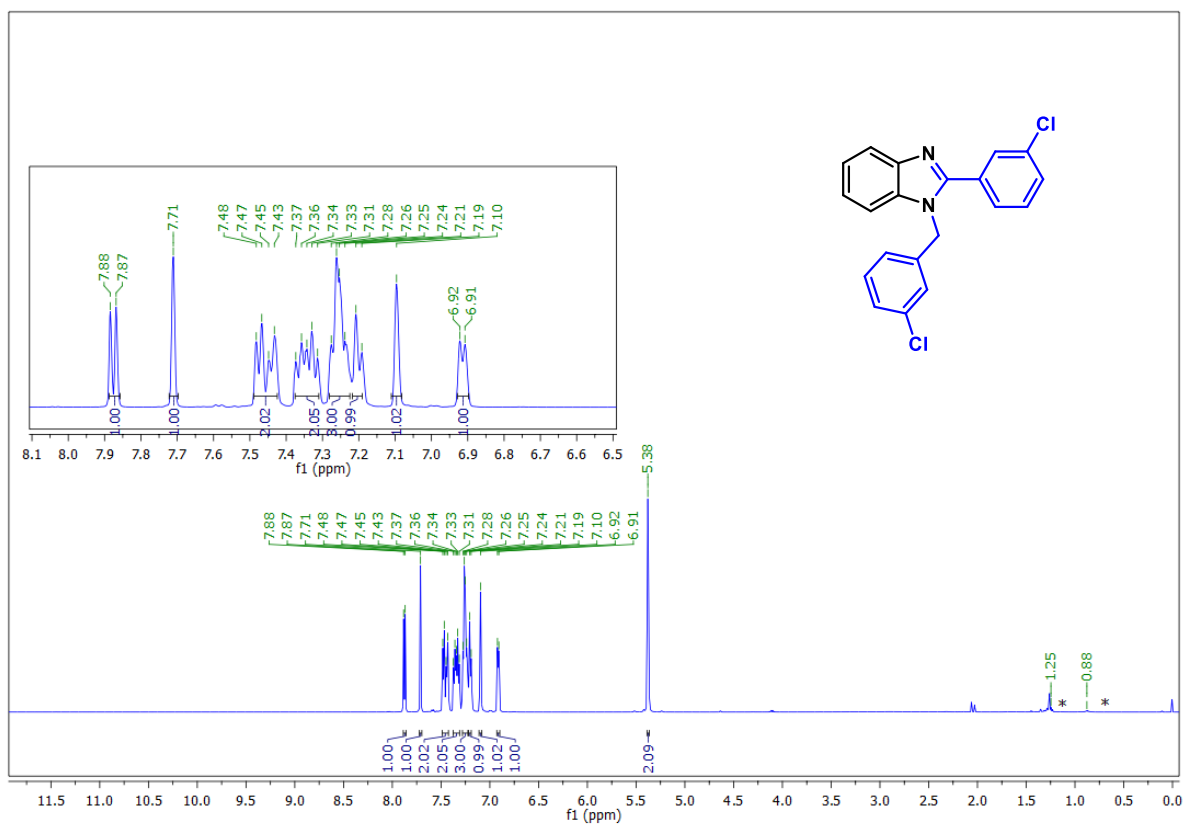
**Fig S24.**  $^1\text{H}$  NMR spectrum of **6g** (in  $\text{CDCl}_3$  solvent) (#acetone, \*hexane).



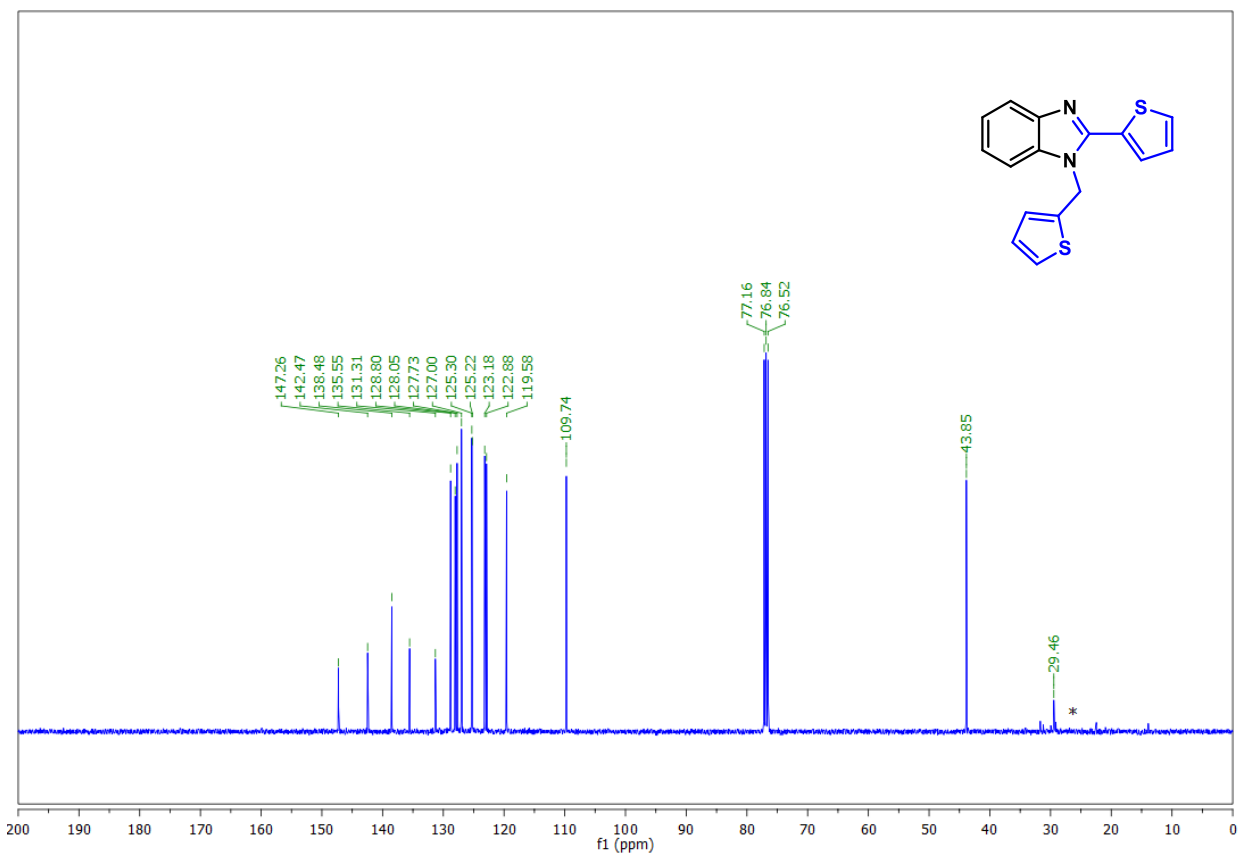
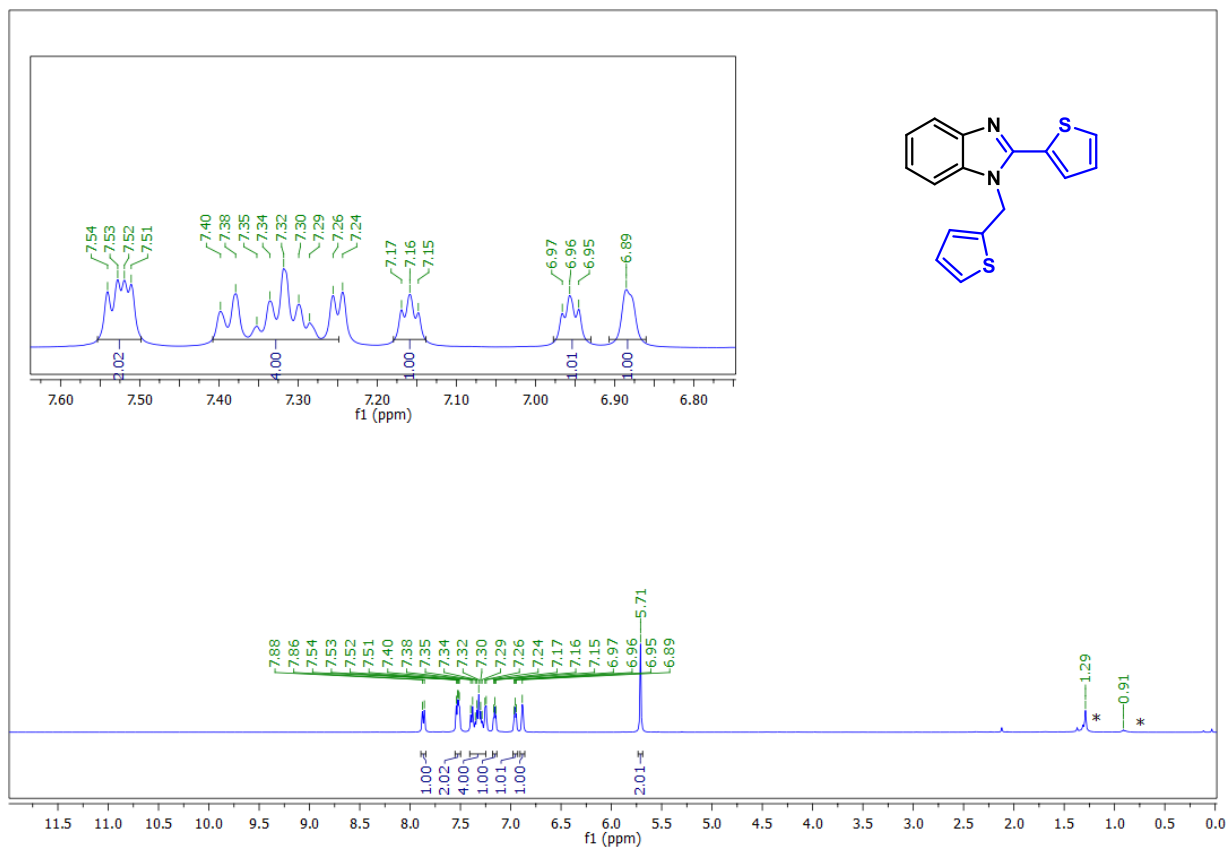
**Fig S25.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6h** (in CDCl<sub>3</sub> solvent) (\*hexane).



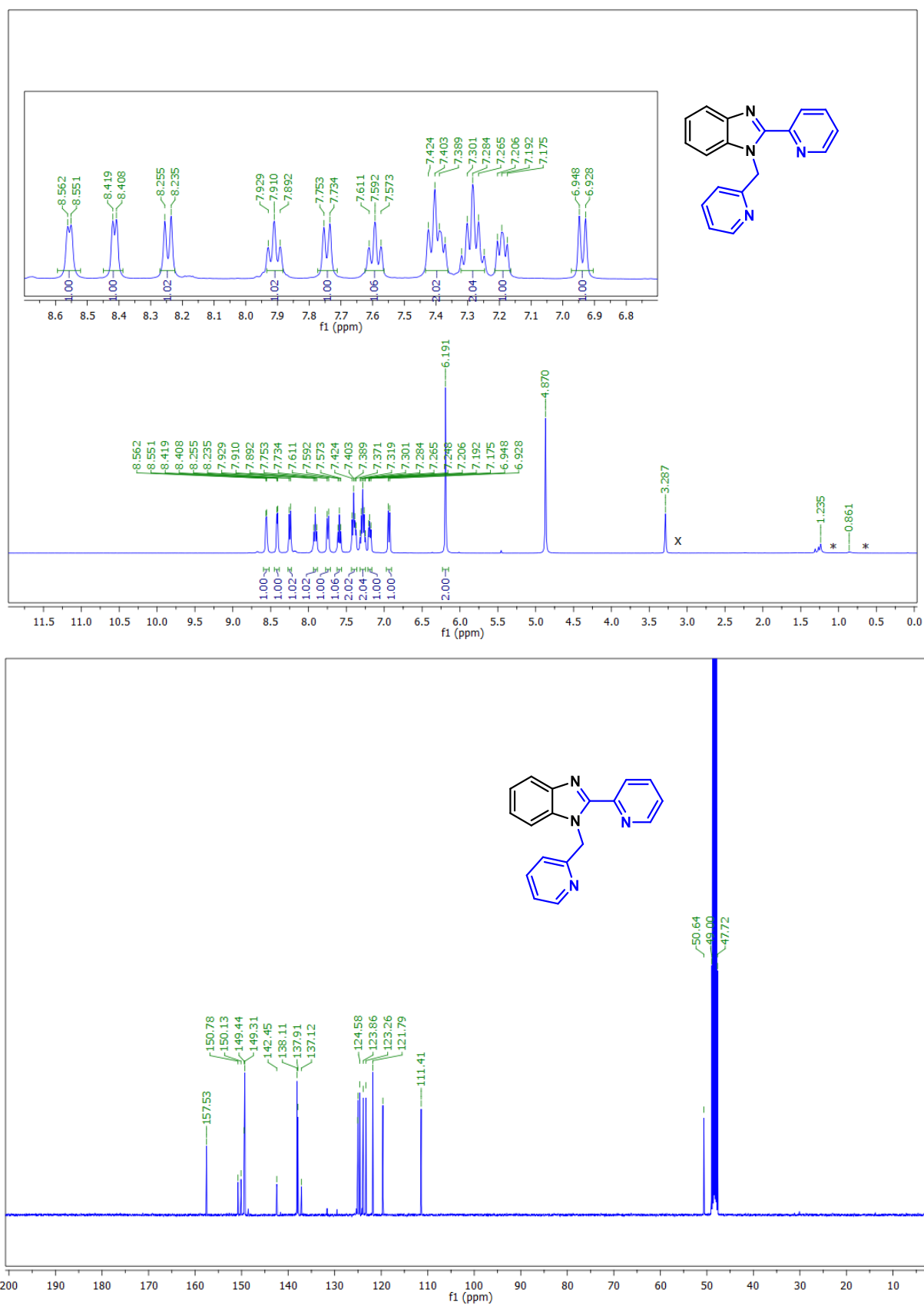
**Fig S26.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6i** (in CDCl<sub>3</sub> solvent) (\*<sup>1</sup>hexane).



**Fig S27.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6j** (in CDCl<sub>3</sub> solvent) (\*hexane).

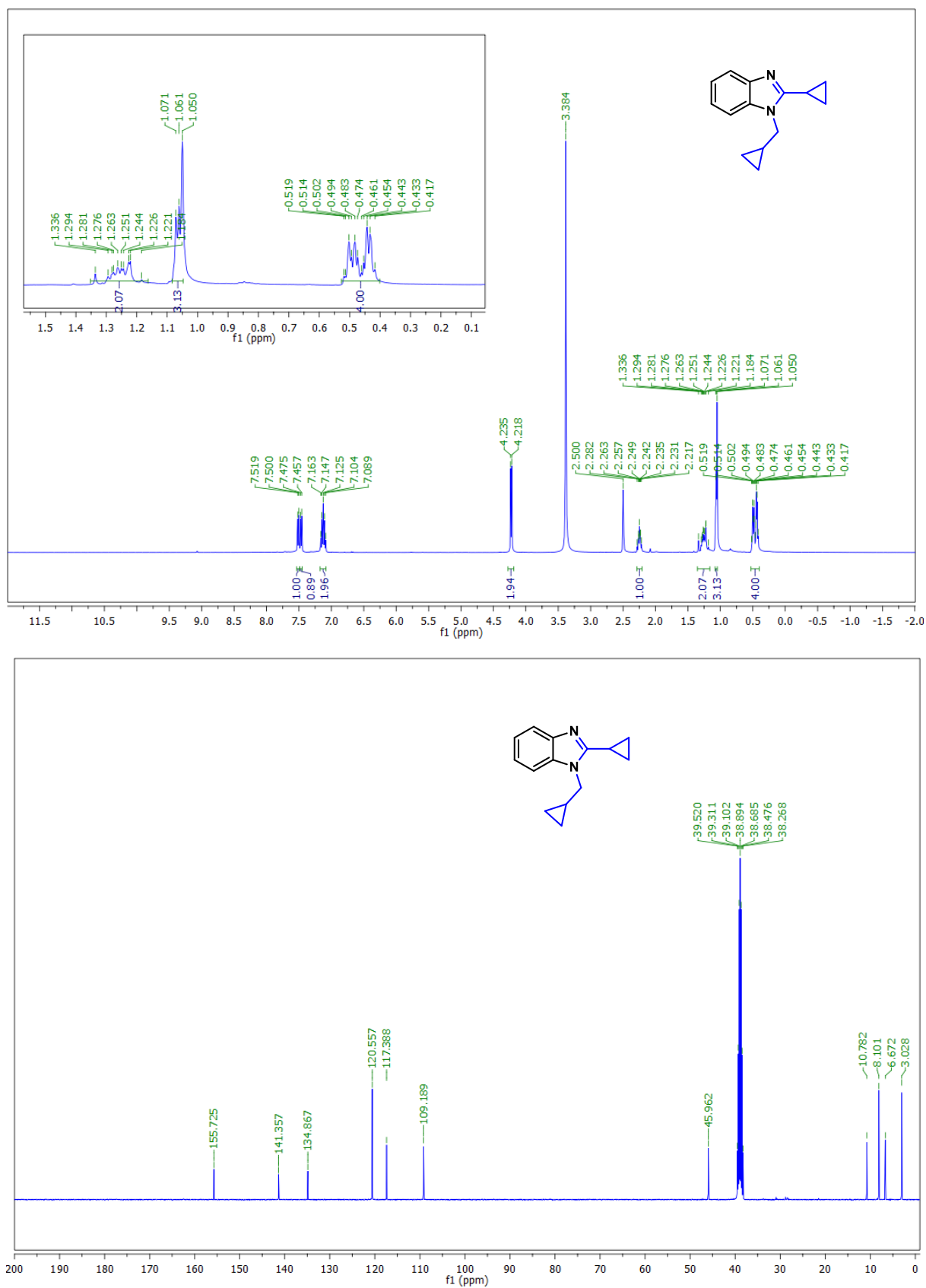


**Fig S28.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6k** (in CDCl<sub>3</sub> solvent) (\*hexane).

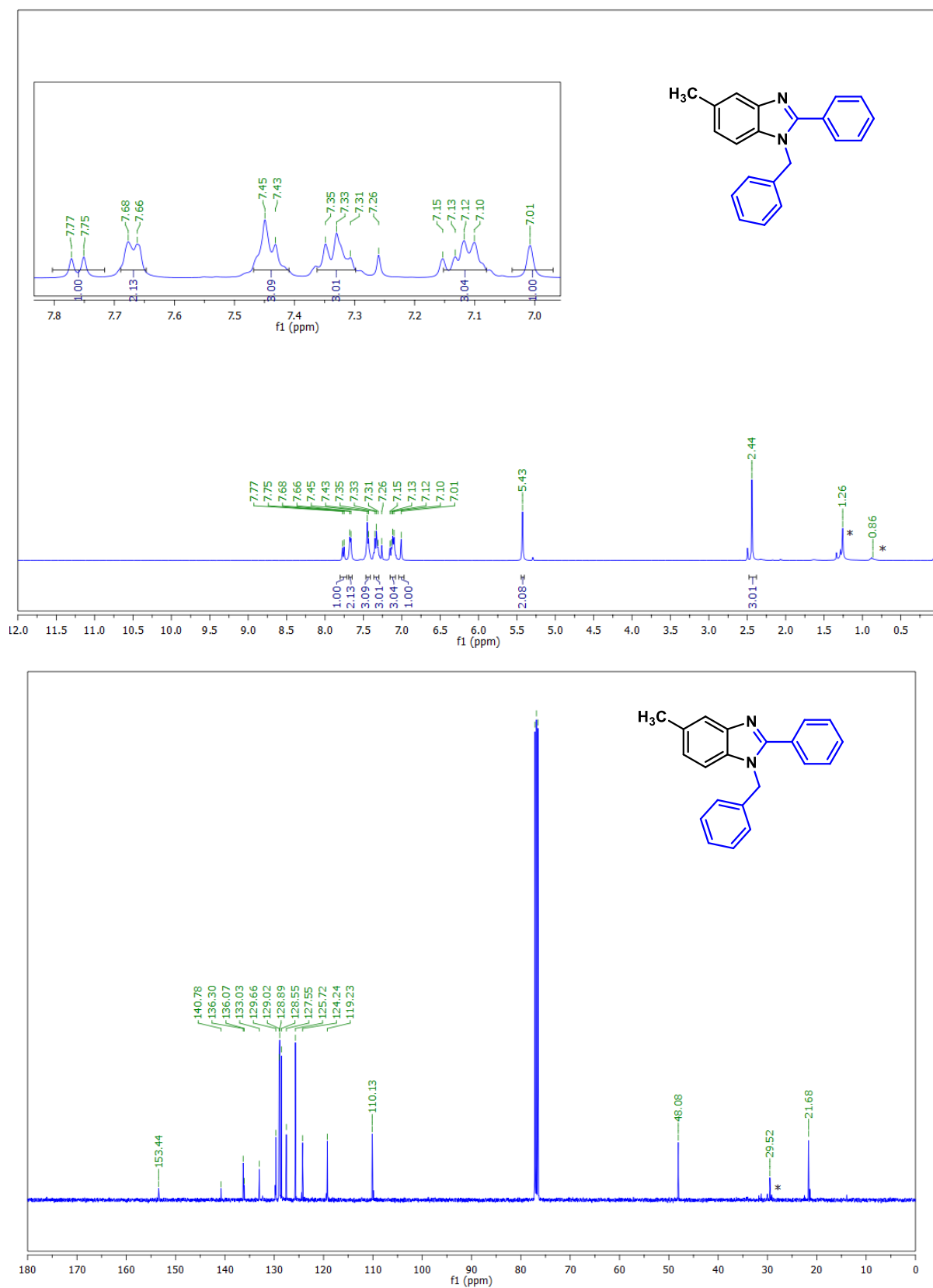


**Fig S29.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **61** (in CD<sub>3</sub>OD solvent) (X water, \*hexane).

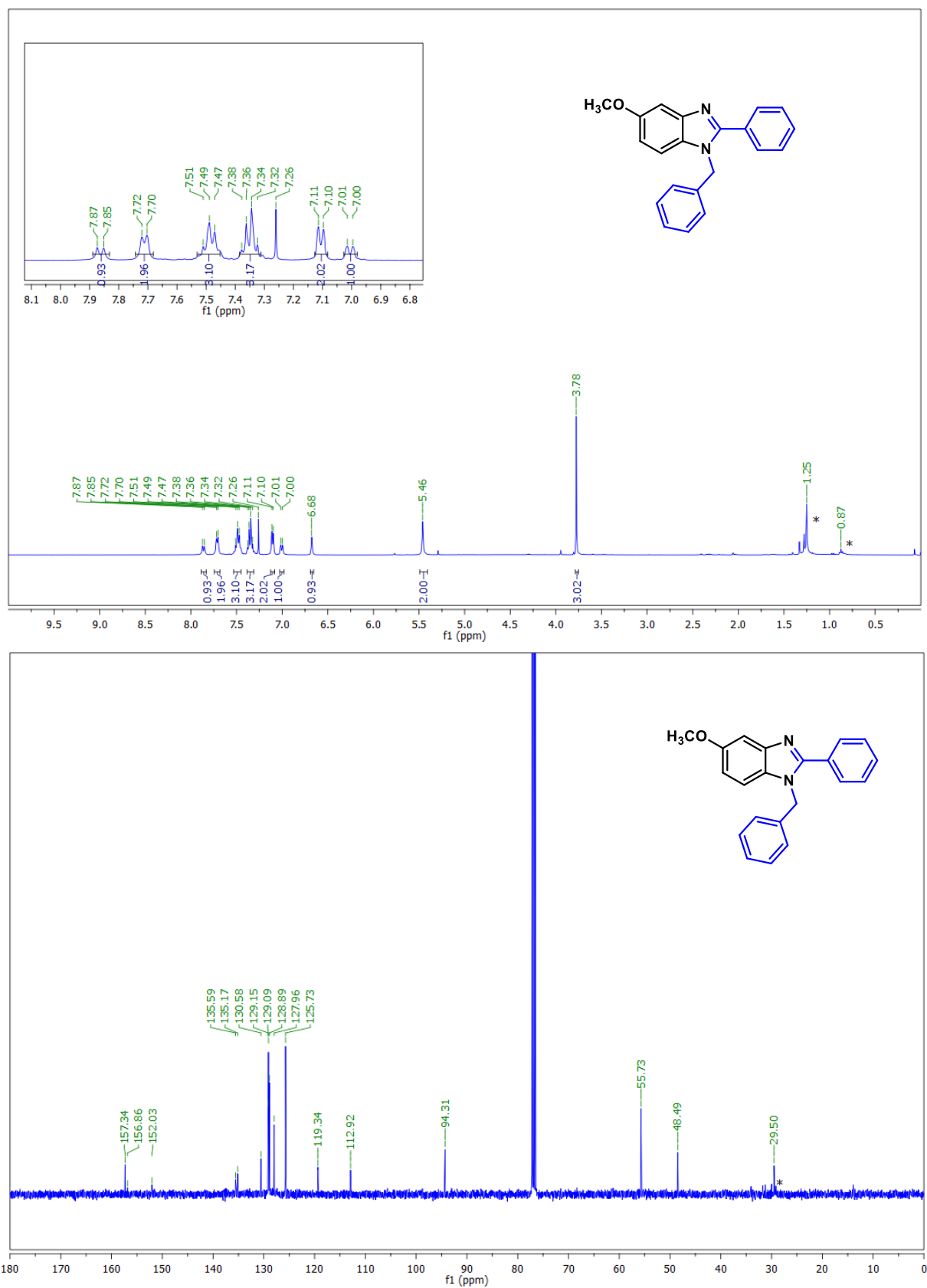




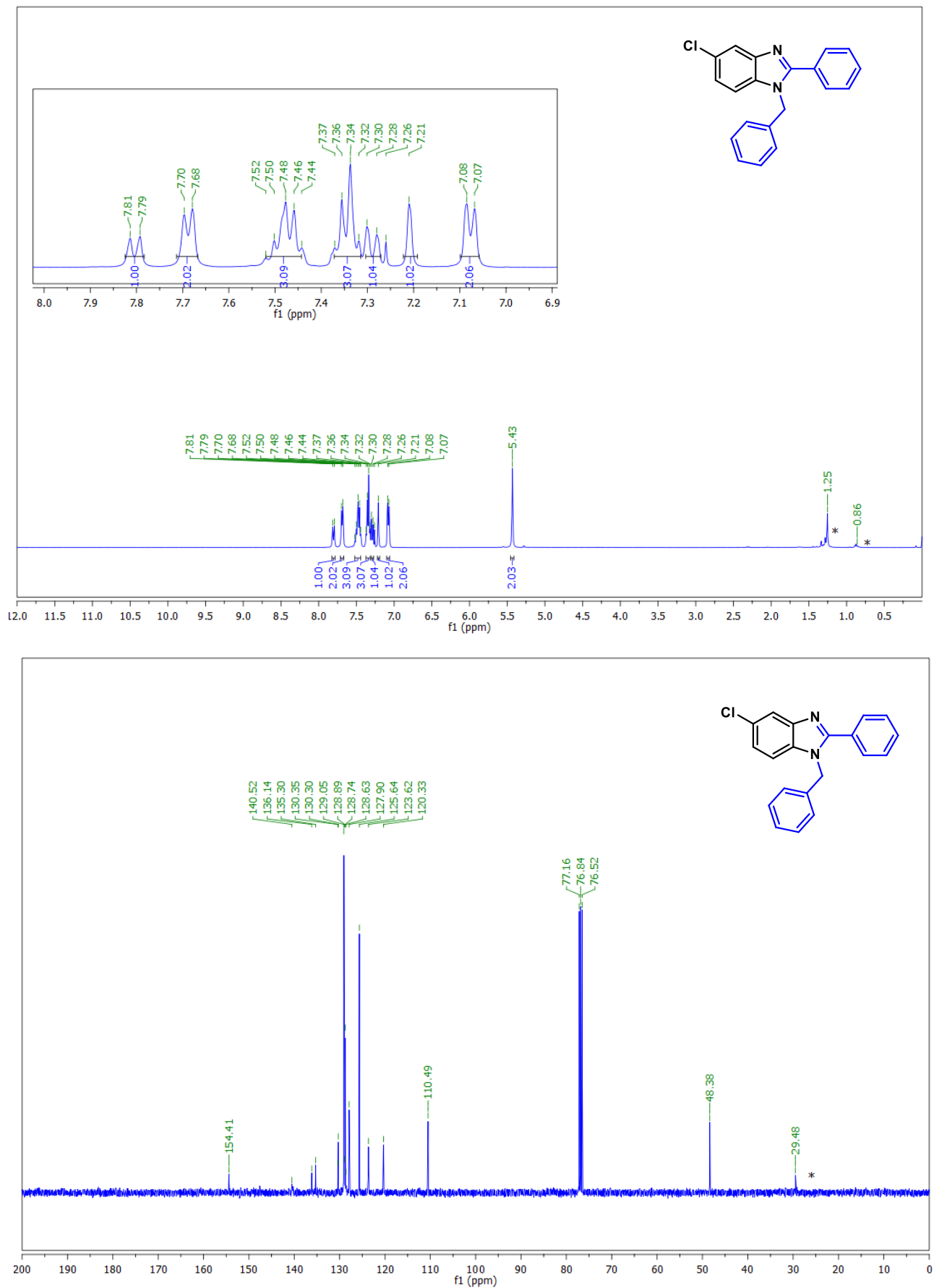
**Fig S30.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6m** (in DMSO-d<sub>6</sub> solvent).



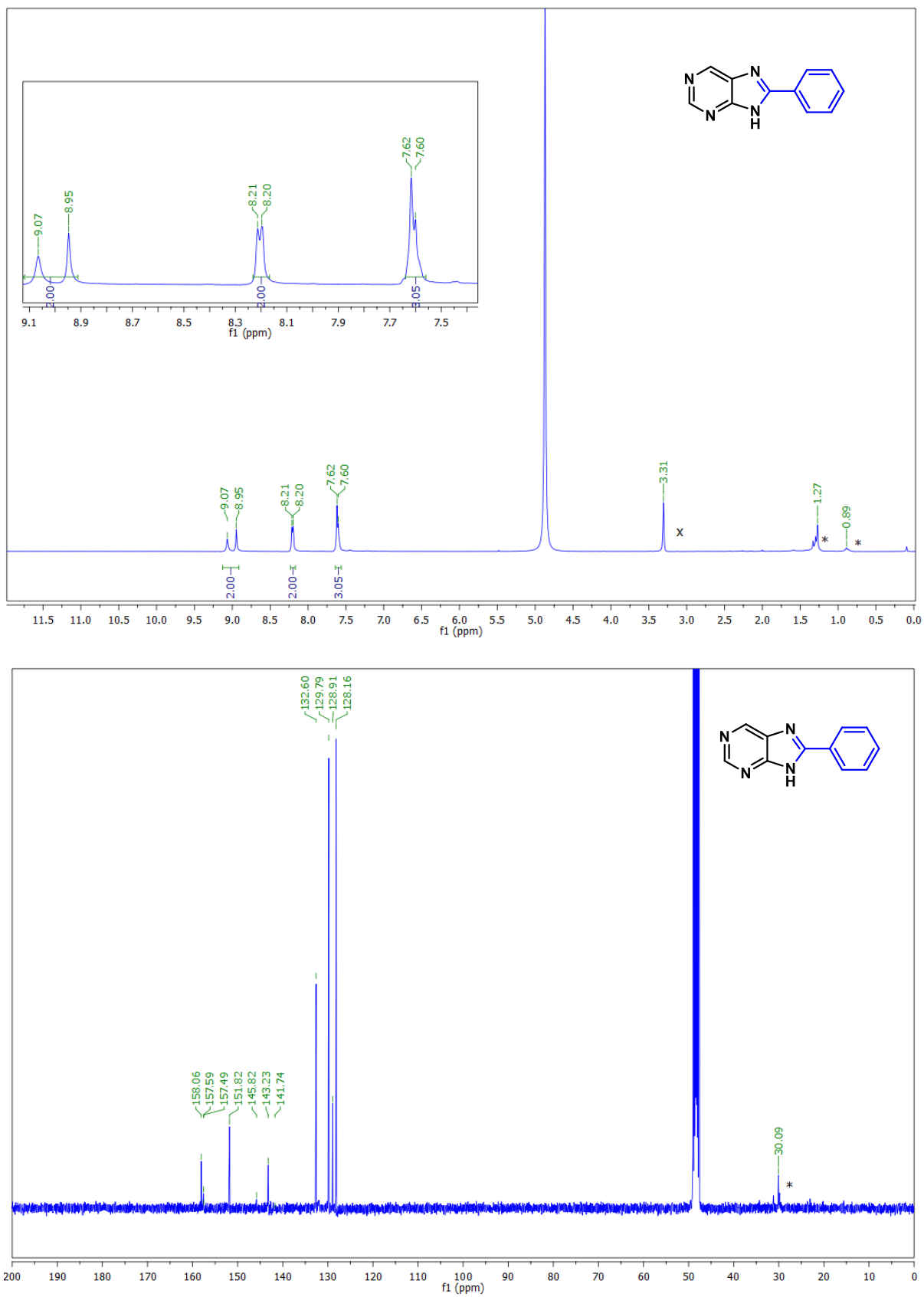
**Fig S31.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6n** (in CDCl<sub>3</sub> solvent) (\*hexane).



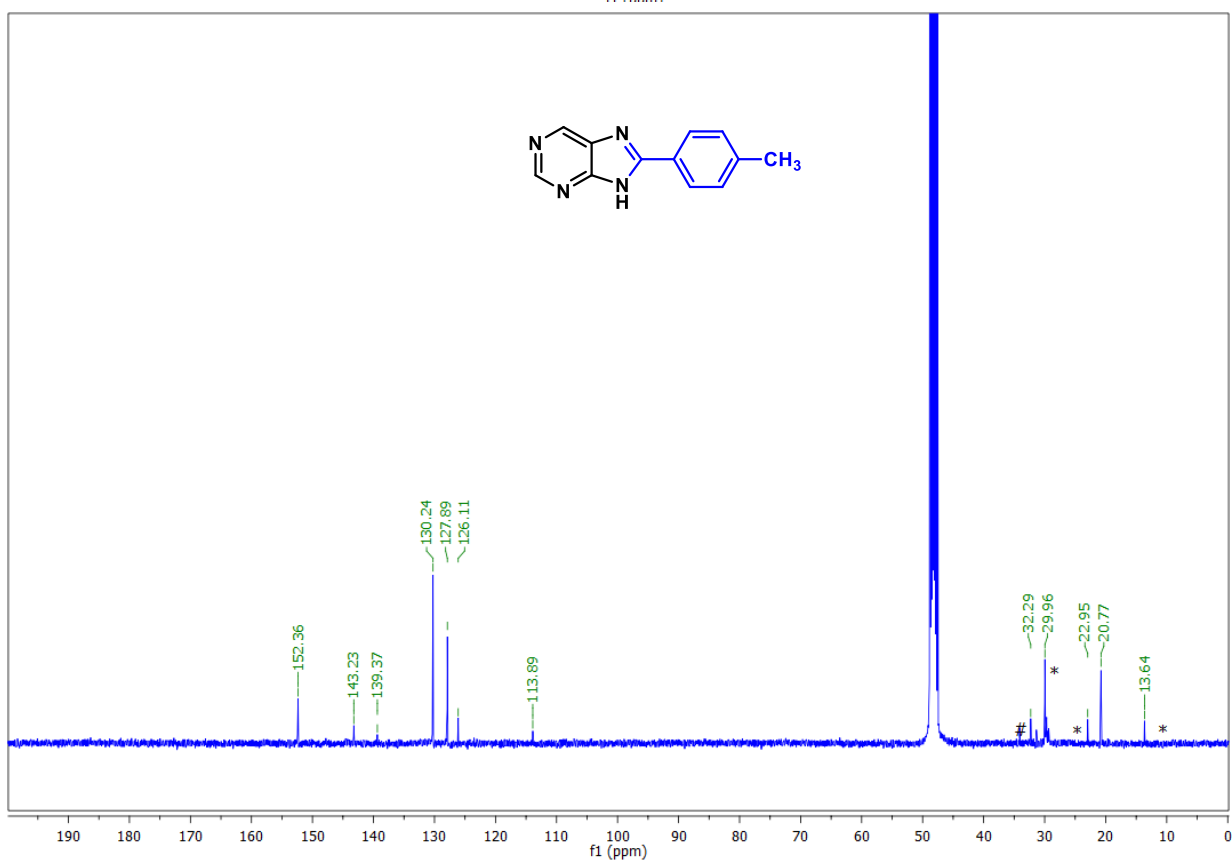
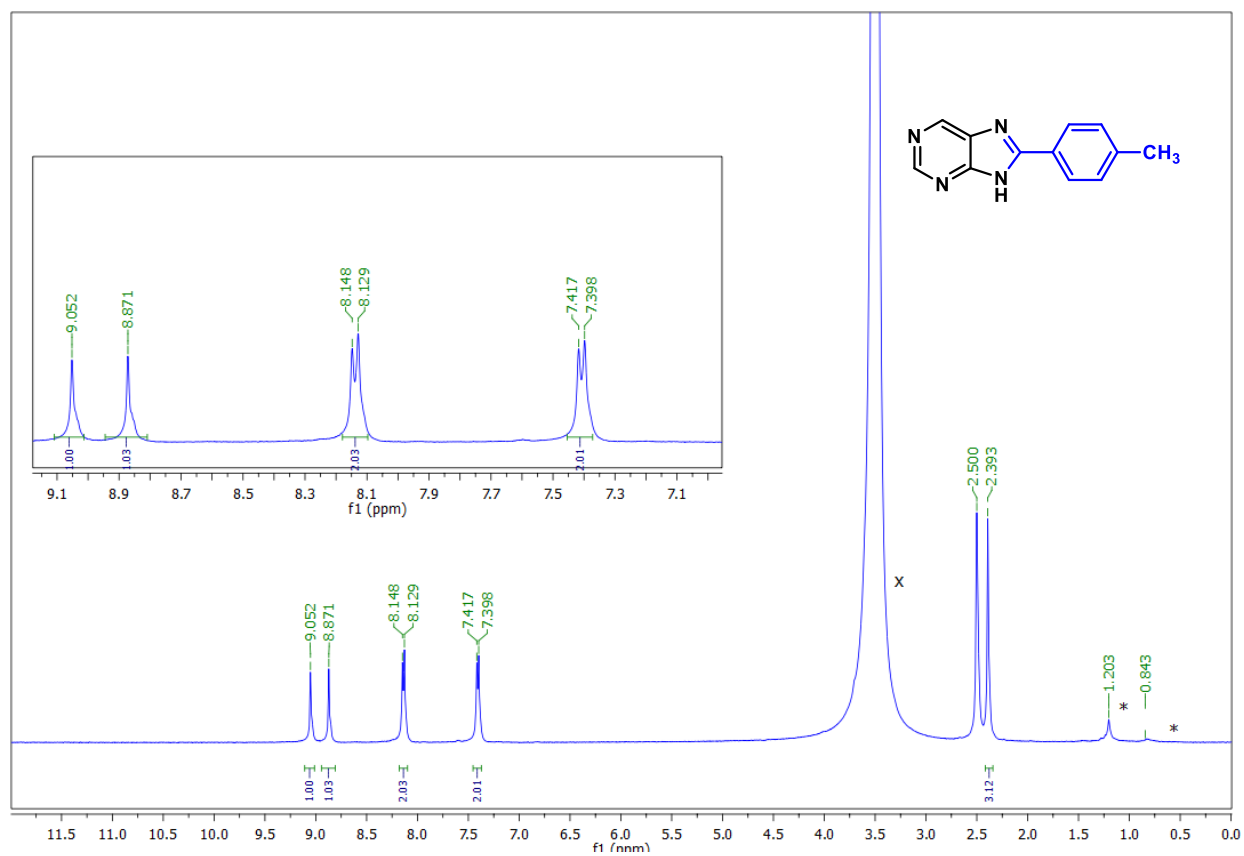
**Fig S32.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **60** (in CDCl<sub>3</sub> solvent, \*hexane).



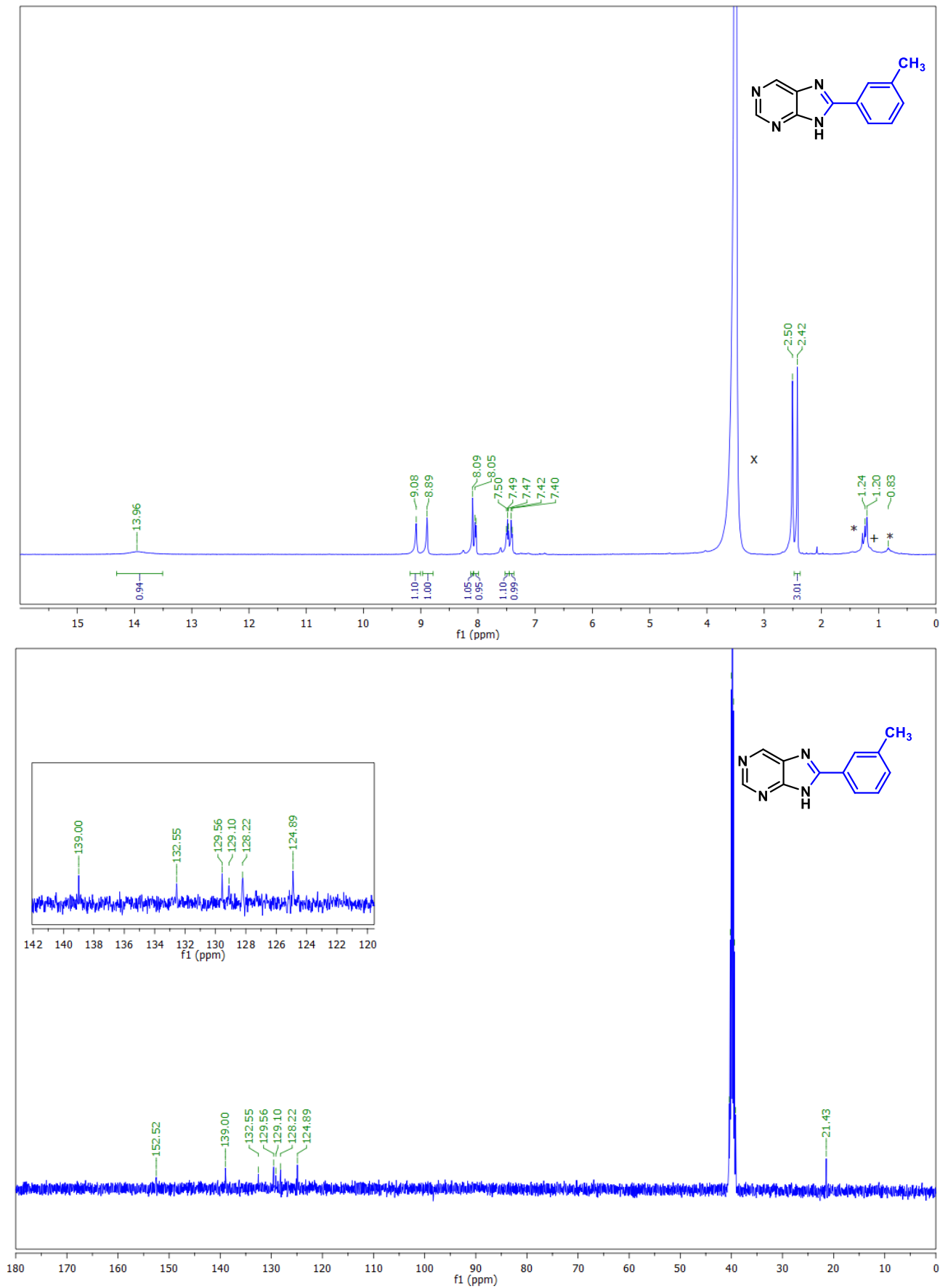
**Fig S33.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6p** (in CDCl<sub>3</sub> solvent, \* hexane).



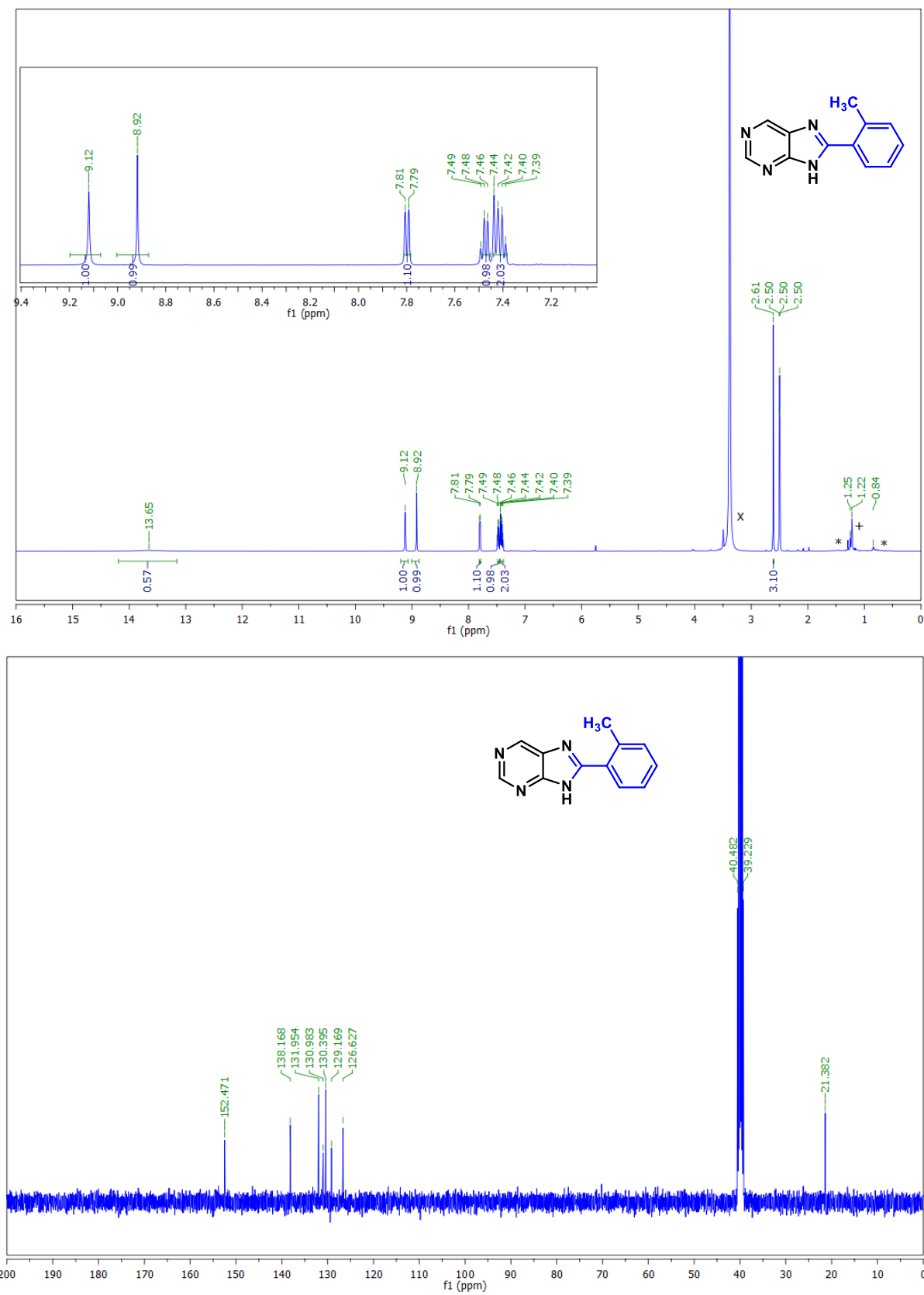
**Fig S34.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **10a** (in CD<sub>3</sub>OD solvent) (x water, \*hexane).



**Fig S35.** <sup>1</sup>H (in DMSO-d<sub>6</sub> solvent) and <sup>13</sup>C NMR spectra of **10b** (in CD<sub>3</sub>OD solvent) (x water, # acetone, \* hexane).

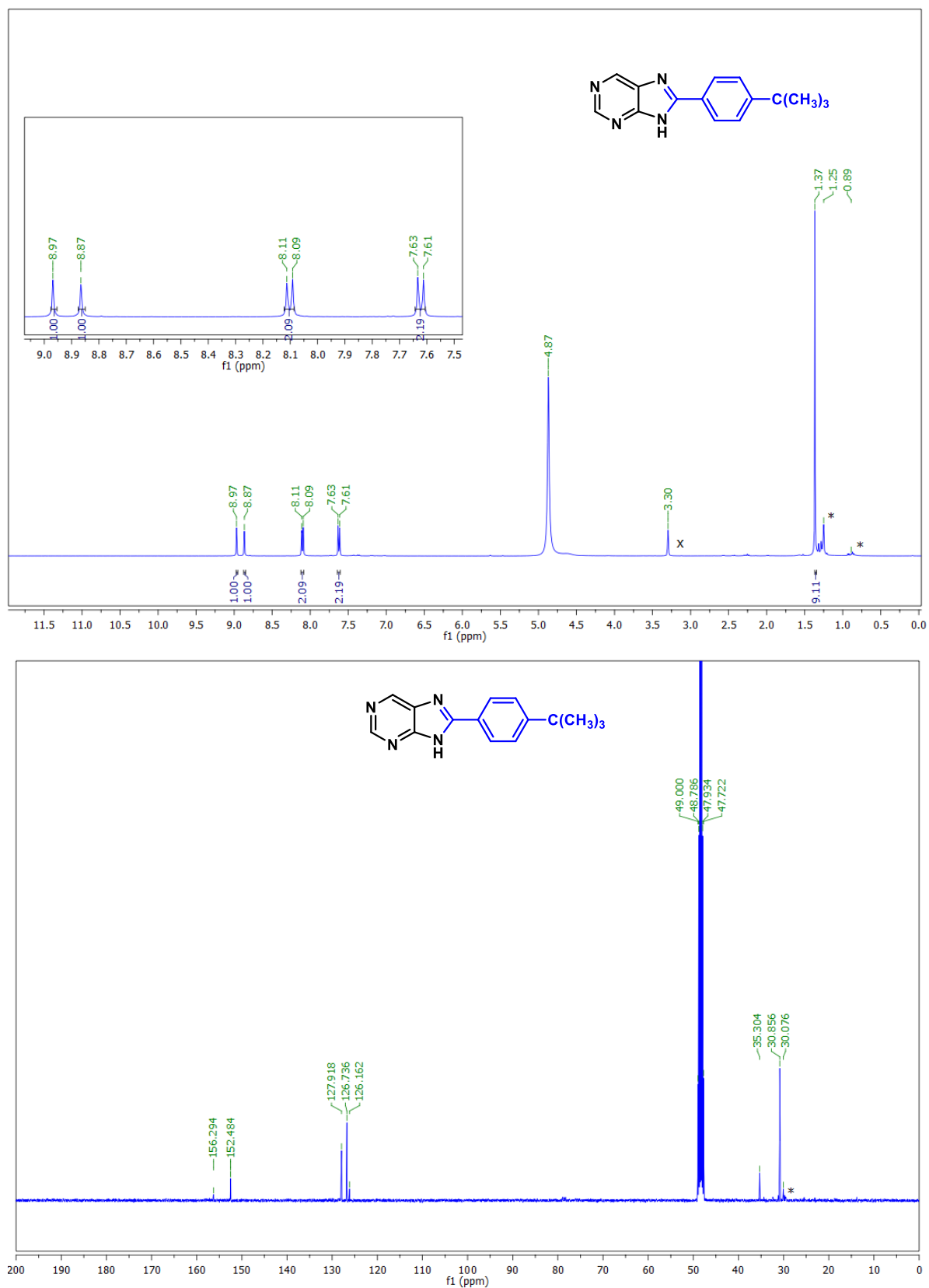


**Fig S36.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **10c** (in DMSO-d<sub>6</sub> solvent) (X water, +ethylacetate, \*hexane).

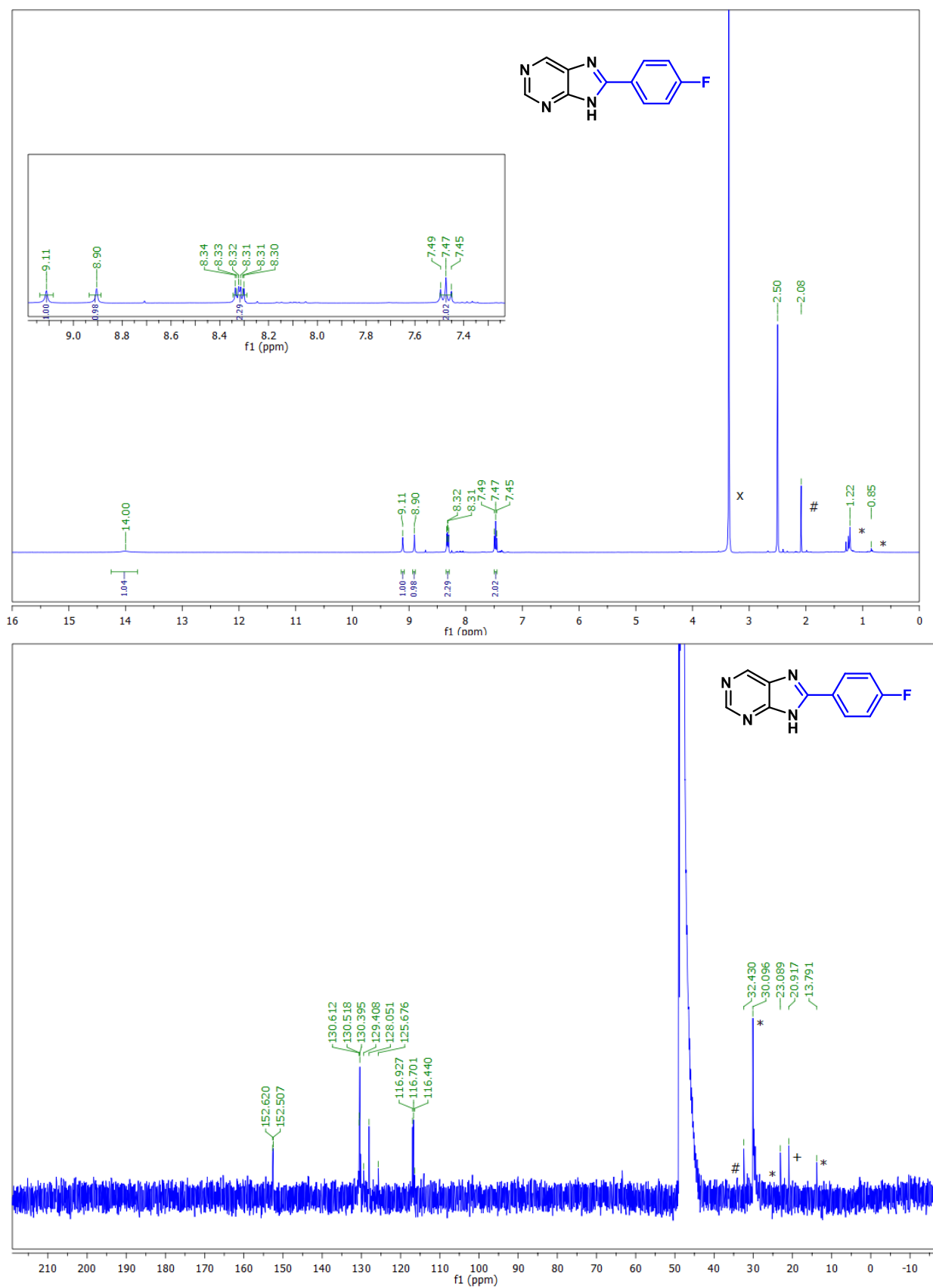


**Fig S37.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **10d** (in DMSO-d<sub>6</sub> solvent) (x water, + ethylacetate, \* hexane).

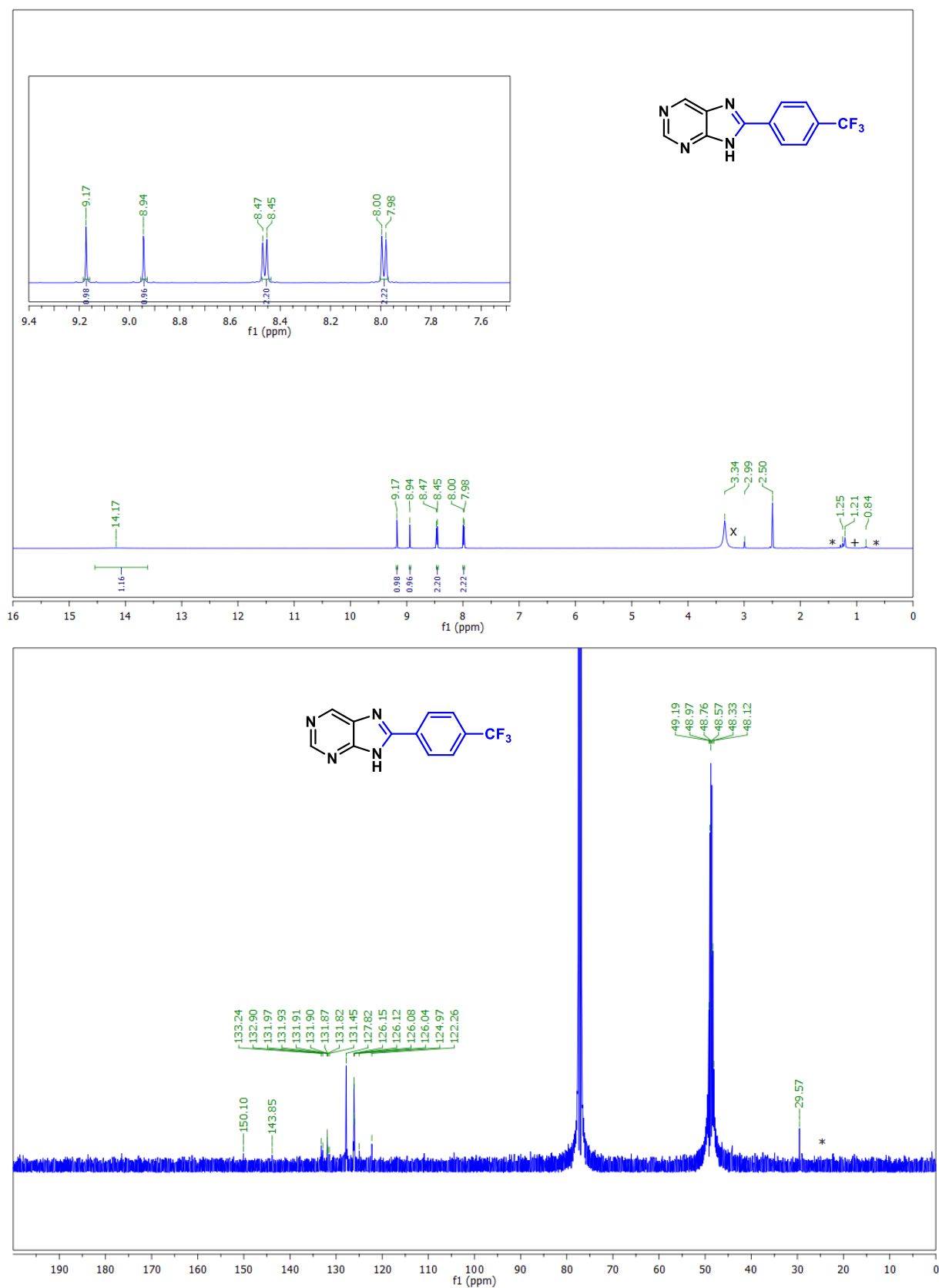




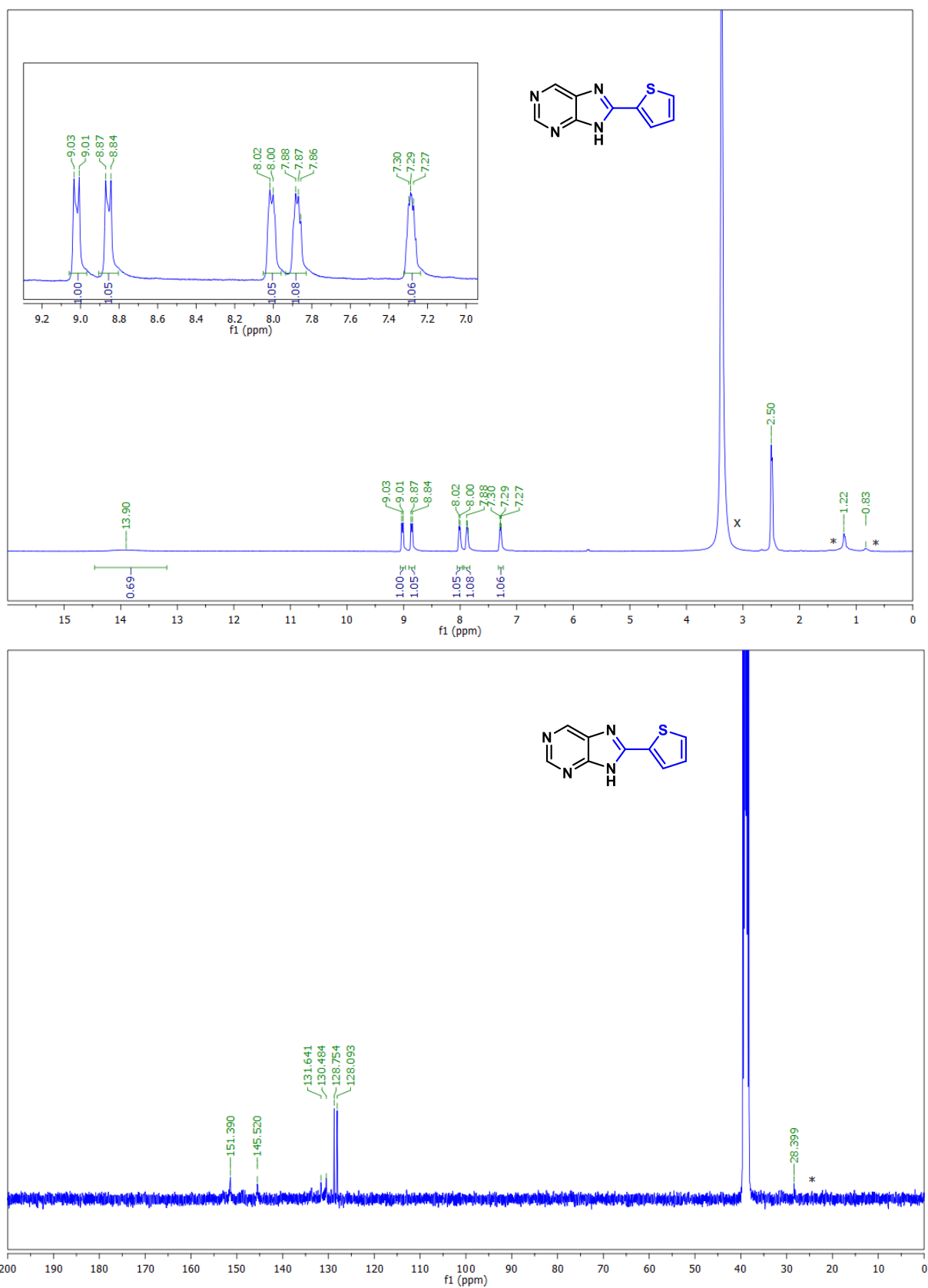
**Fig S38.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **10e** (in CD<sub>3</sub>OD solvent) (\*water, \*hexane).



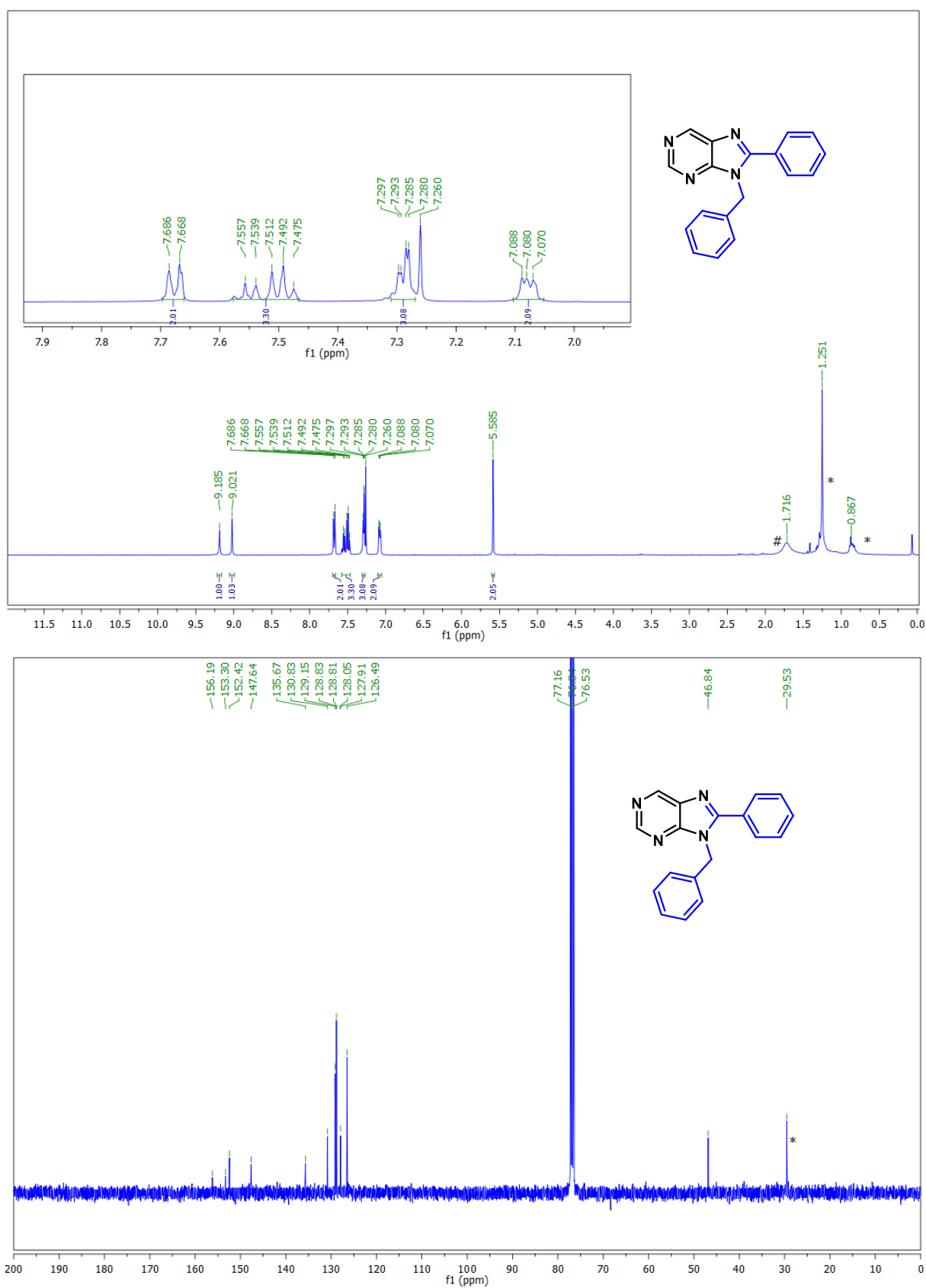
**Fig S39.** <sup>1</sup>H (in DMSO-d<sub>6</sub> solvent) and <sup>13</sup>C (in CD<sub>3</sub>OD solvent) NMR spectra of **10f** (\*water, #acetone, +ethylacetate, \*hexane).



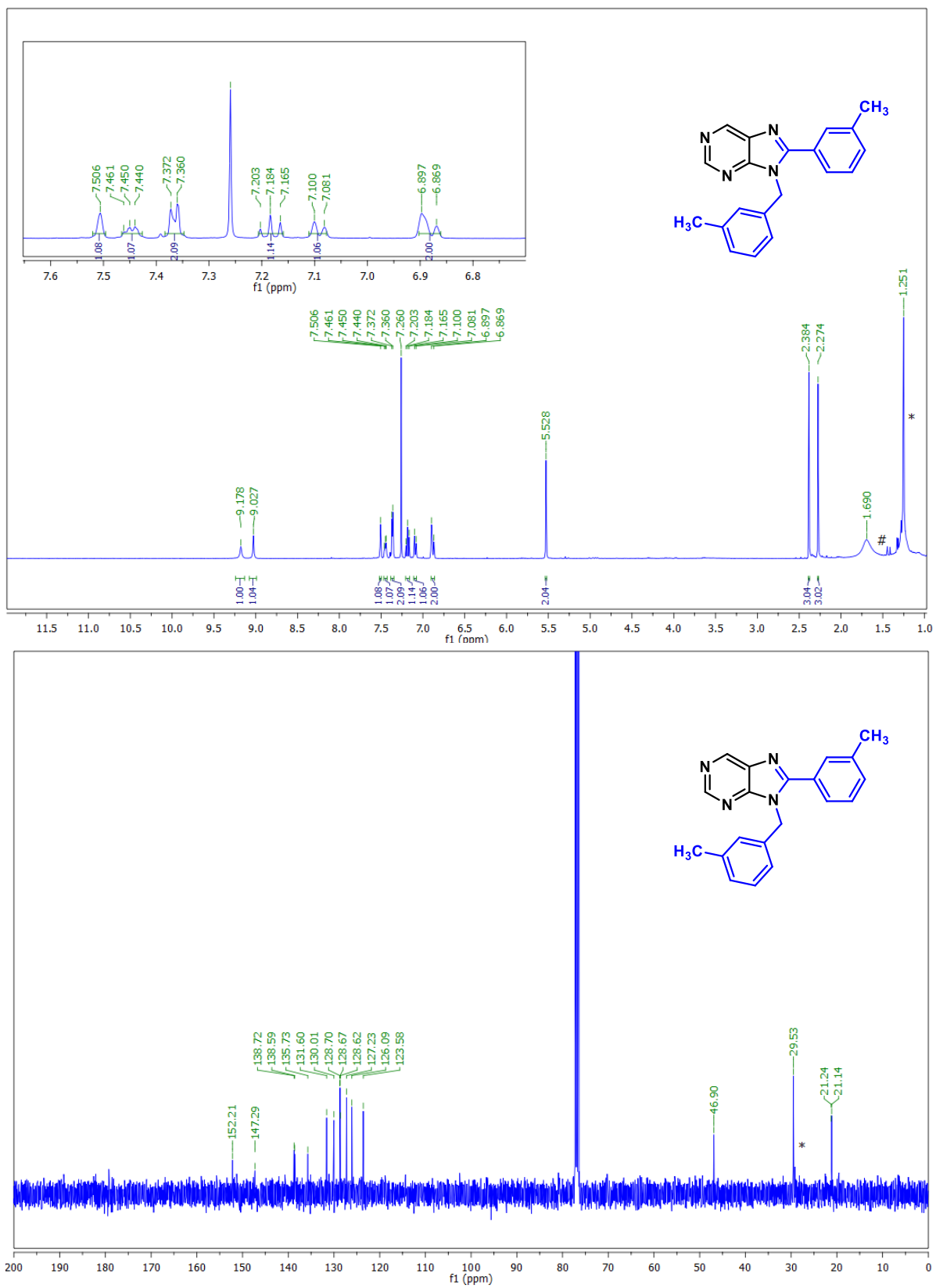
**Fig S40.** <sup>1</sup>H (in DMSO-d<sub>6</sub> solvent) and <sup>13</sup>C (in CDCl<sub>3</sub>+ 1drop CD<sub>3</sub>OD solvent) NMR spectra of **10g** (Xwater, +ethylacetate, \*hexane).



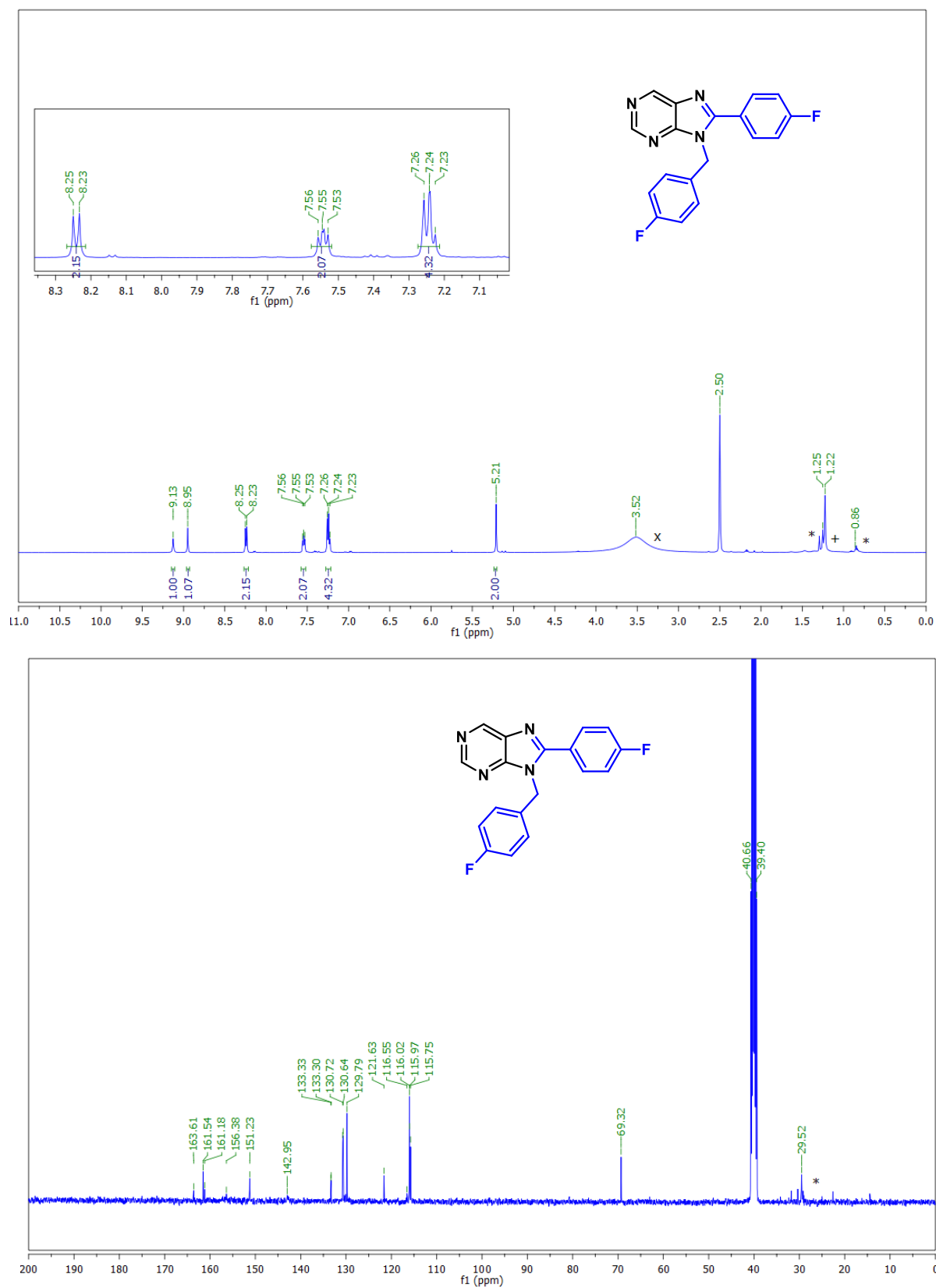
**Fig S41.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **10g** (in DMSO-d<sub>6</sub> solvent) (X water, \*hexane).



**Fig S42.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **11a** (in  $\text{CDCl}_3$  solvent) (# water, \* hexane).



**Fig S43.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **11b** (in CDCl<sub>3</sub> solvent) (#water, \* hexane).



**Fig S44.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **11c** (in DMSO-d<sub>6</sub> solvent) (x water, + ethylacetate, \* hexane).

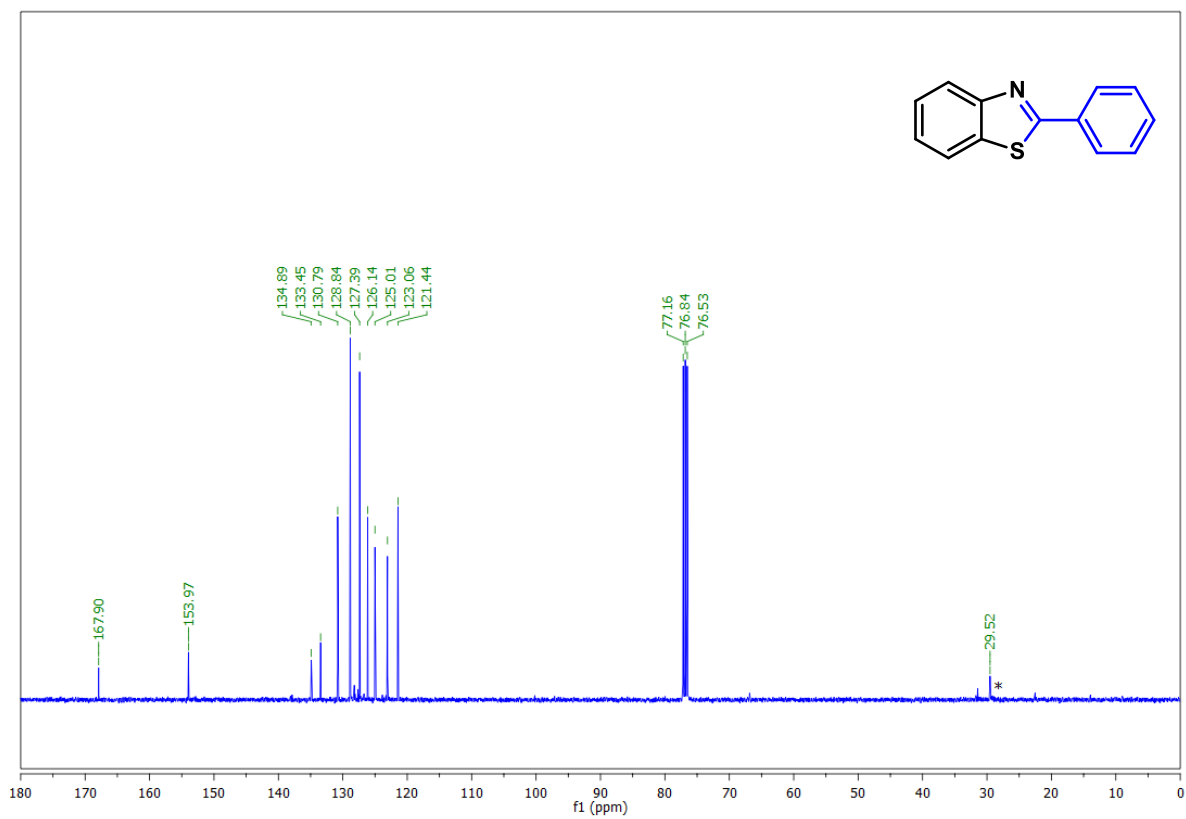
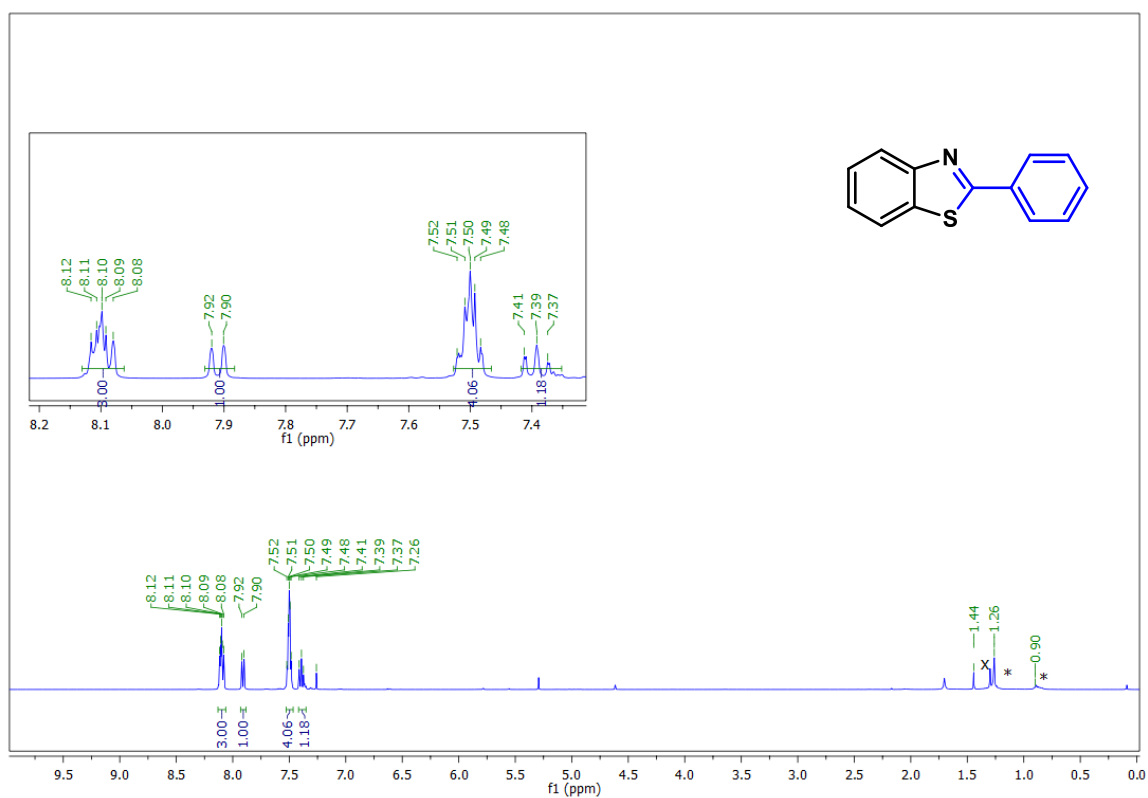
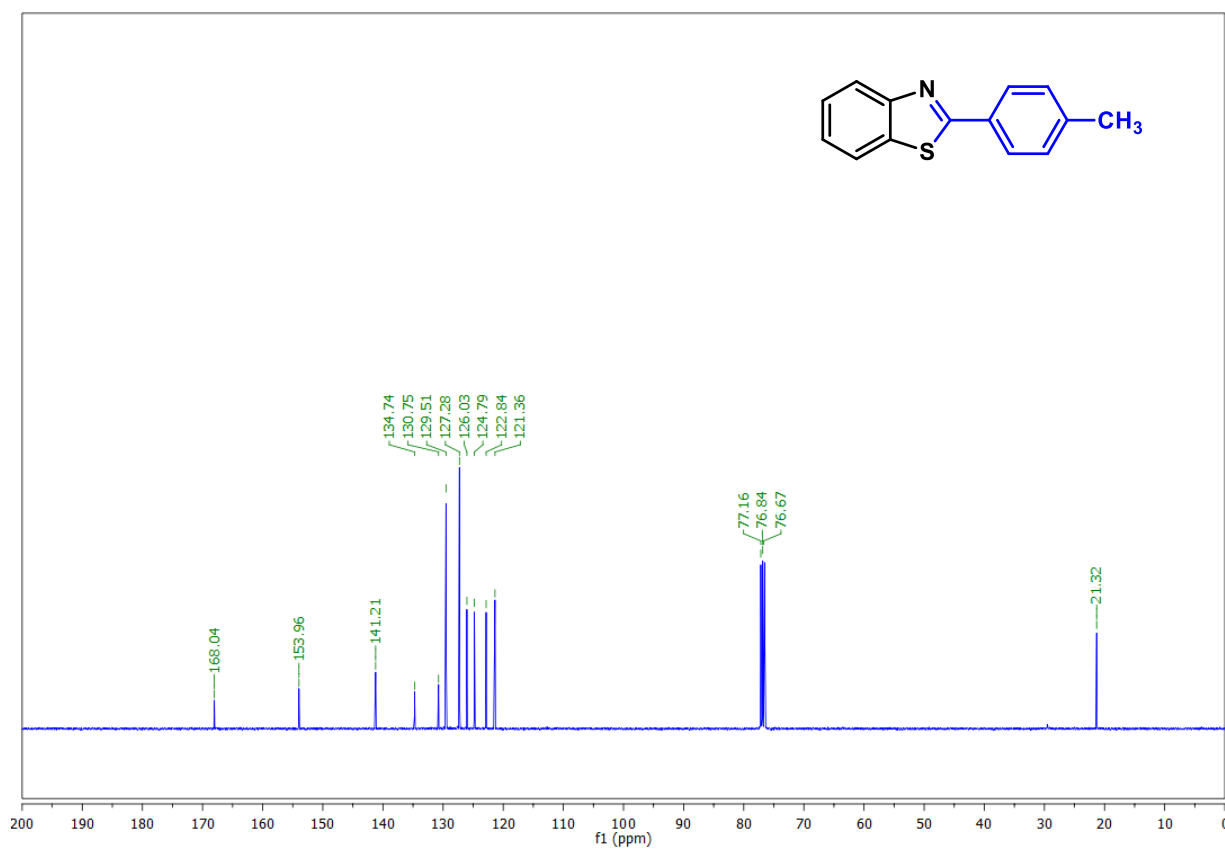
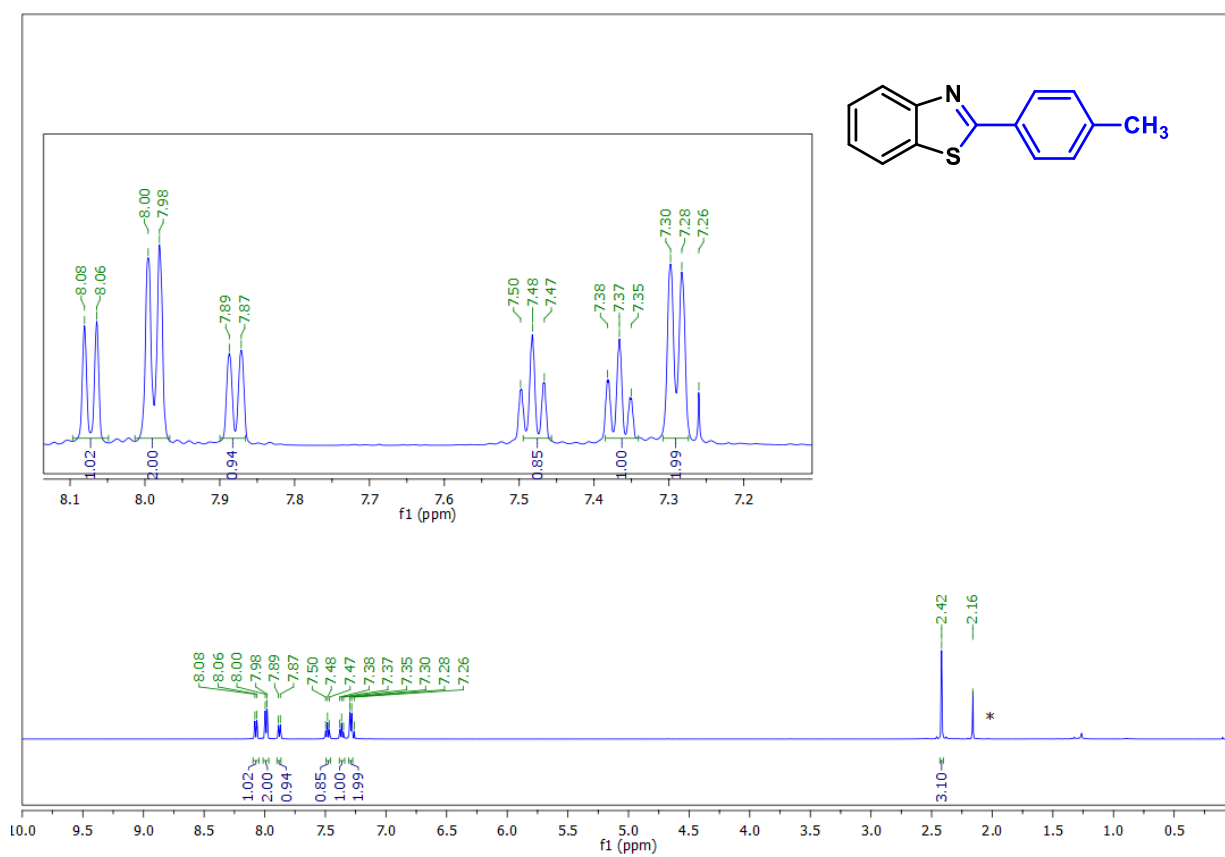
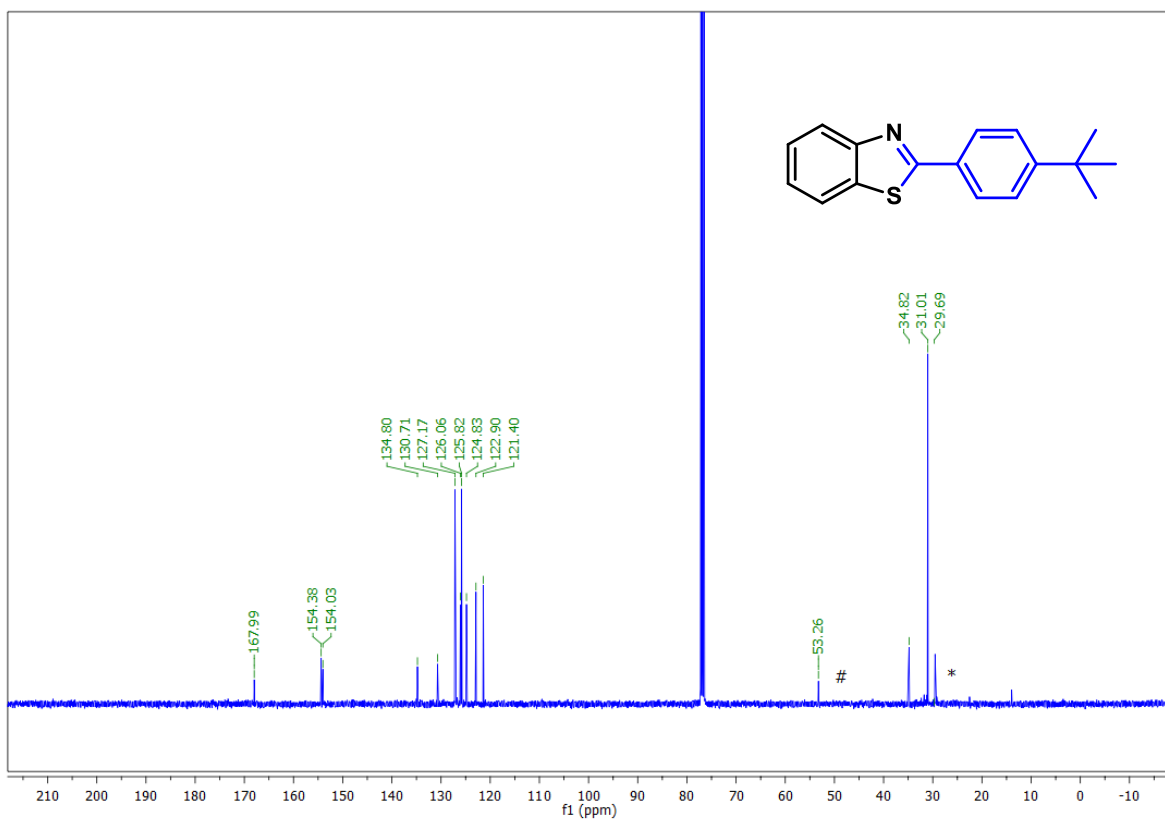
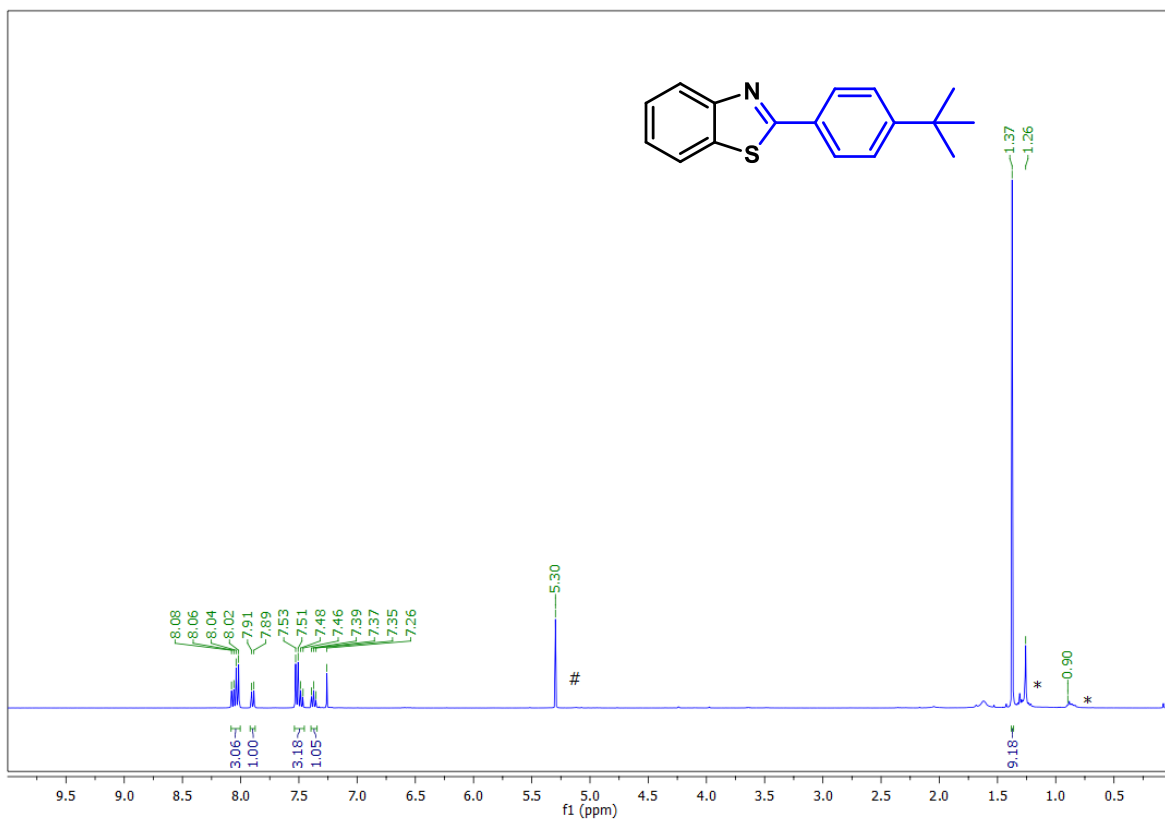


Fig S45.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **12a** (in  $\text{CDCl}_3$  solvent) ( $^x$ water,  $^*$ hexane).

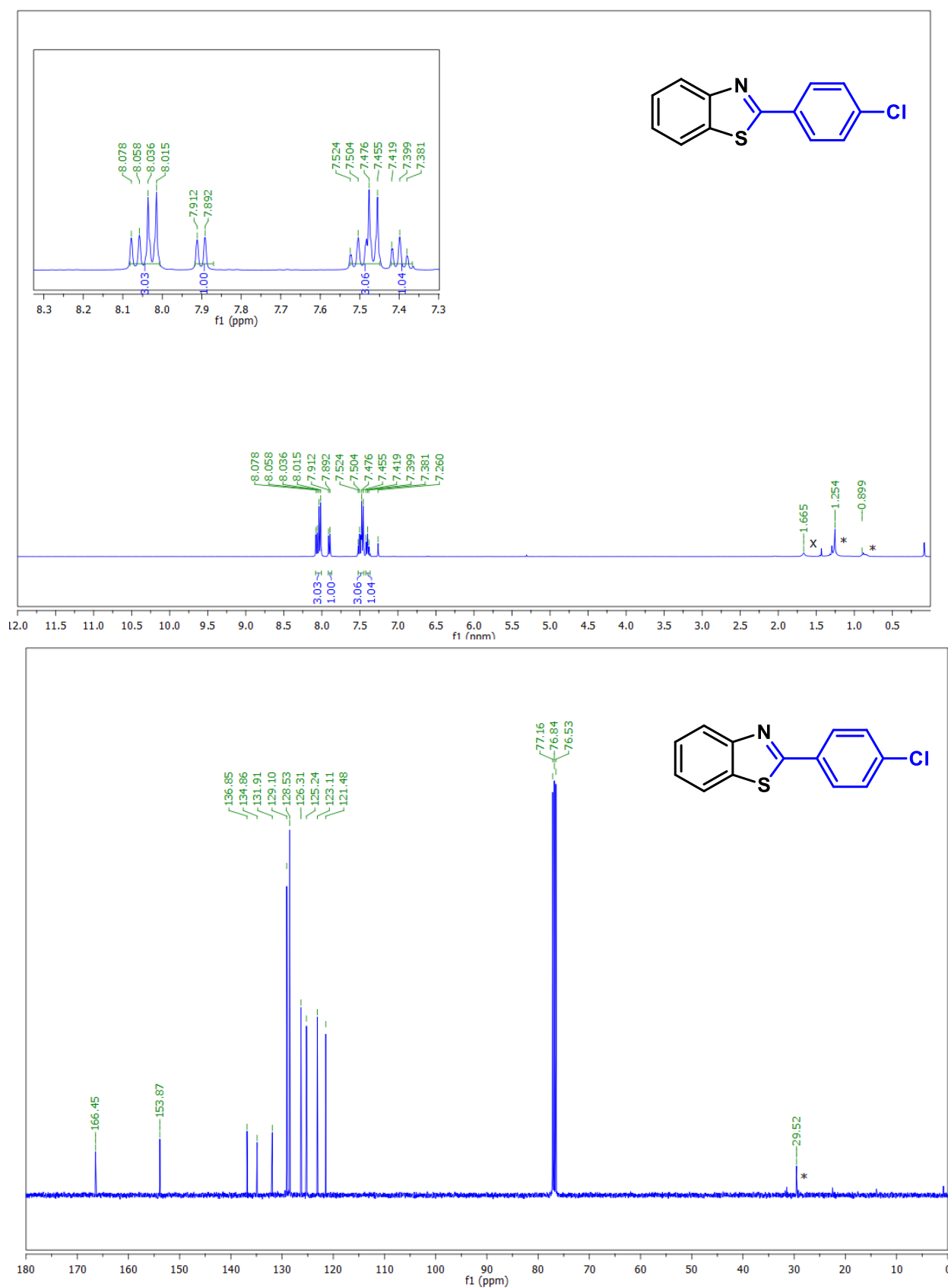




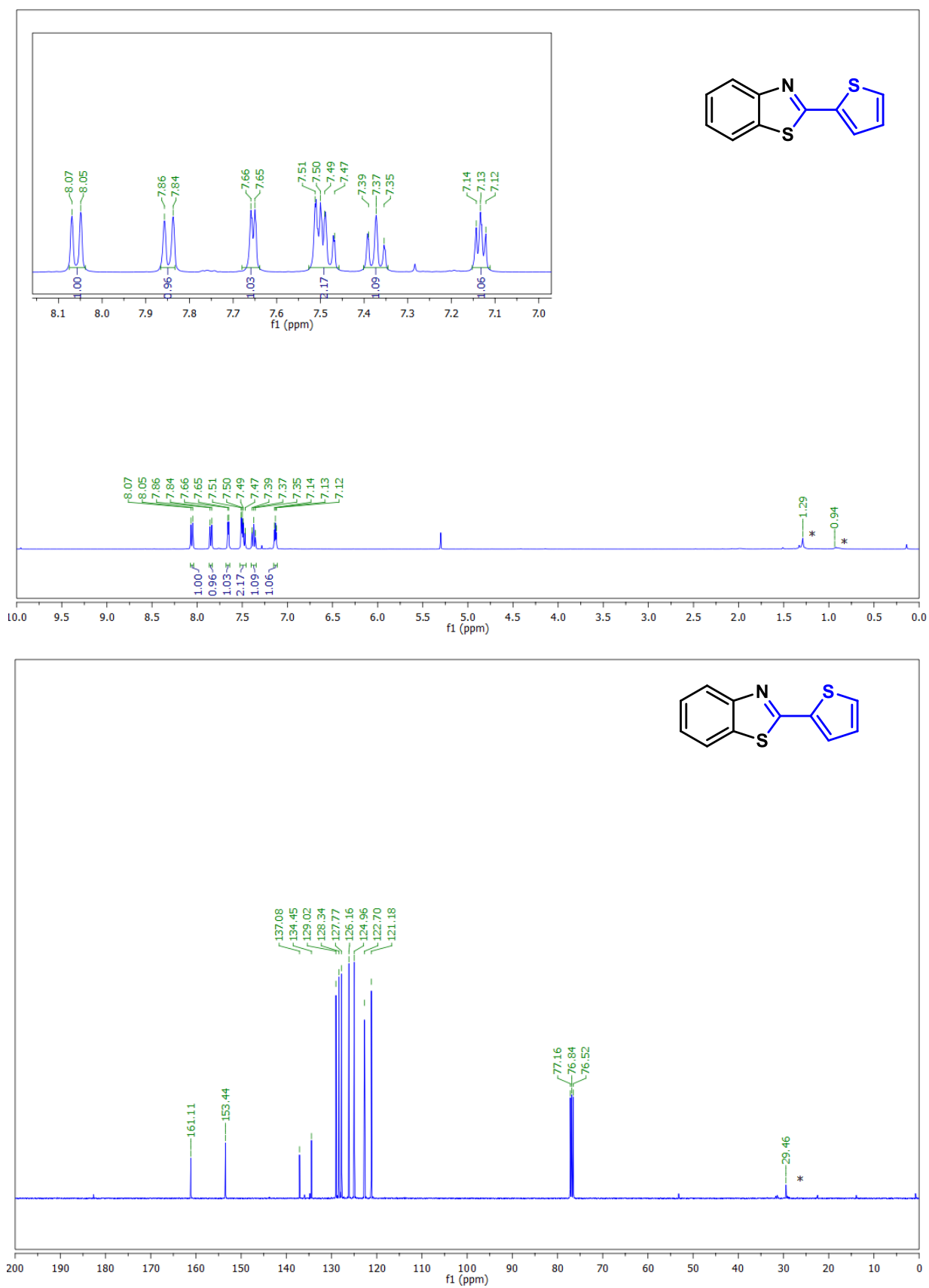
**Fig S46.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **12b** (in CDCl<sub>3</sub> solvent) (\* acetone).



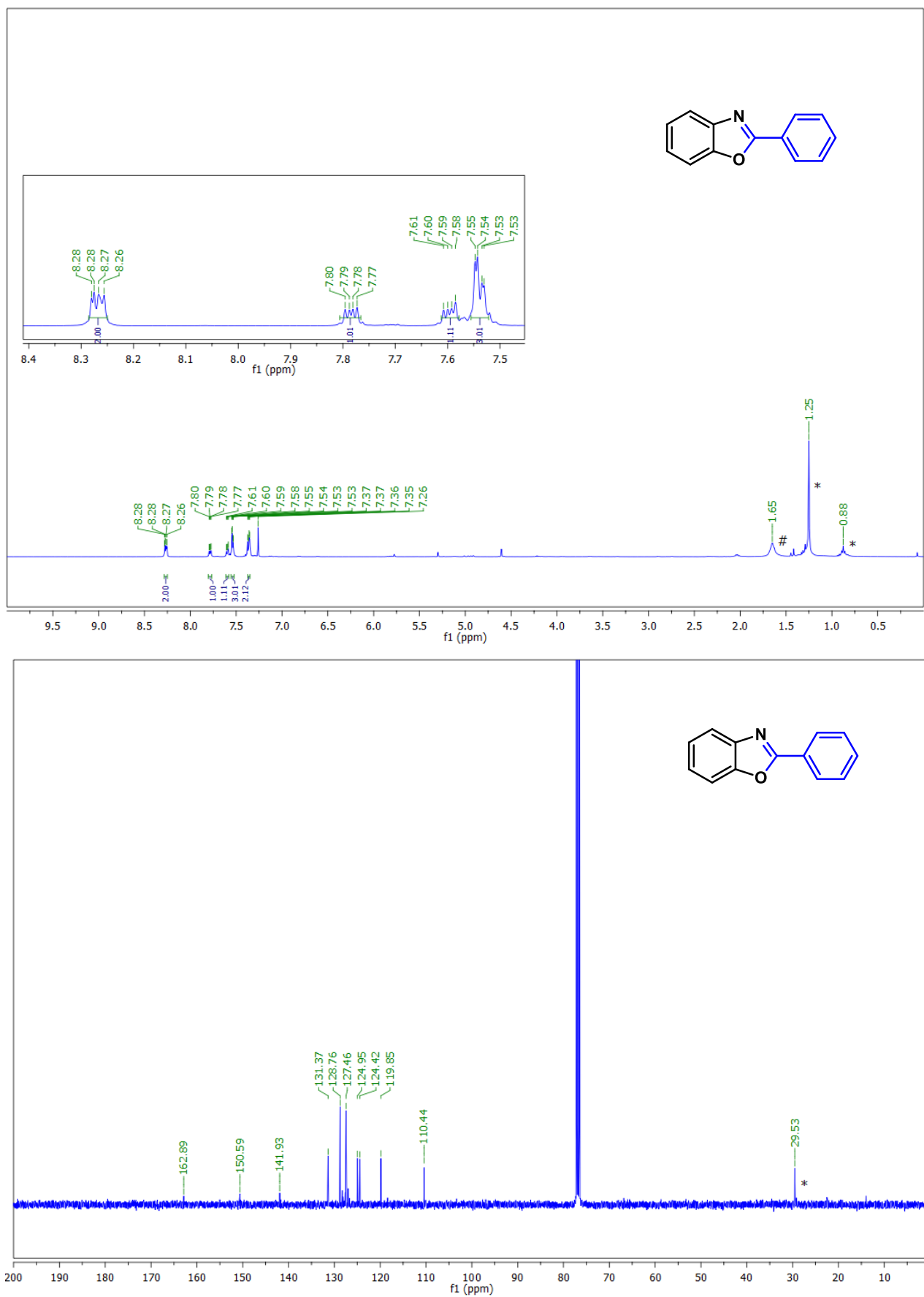
**Fig S47.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **12c** (in CDCl<sub>3</sub> solvent) (\*hexane, # dichloromethane).



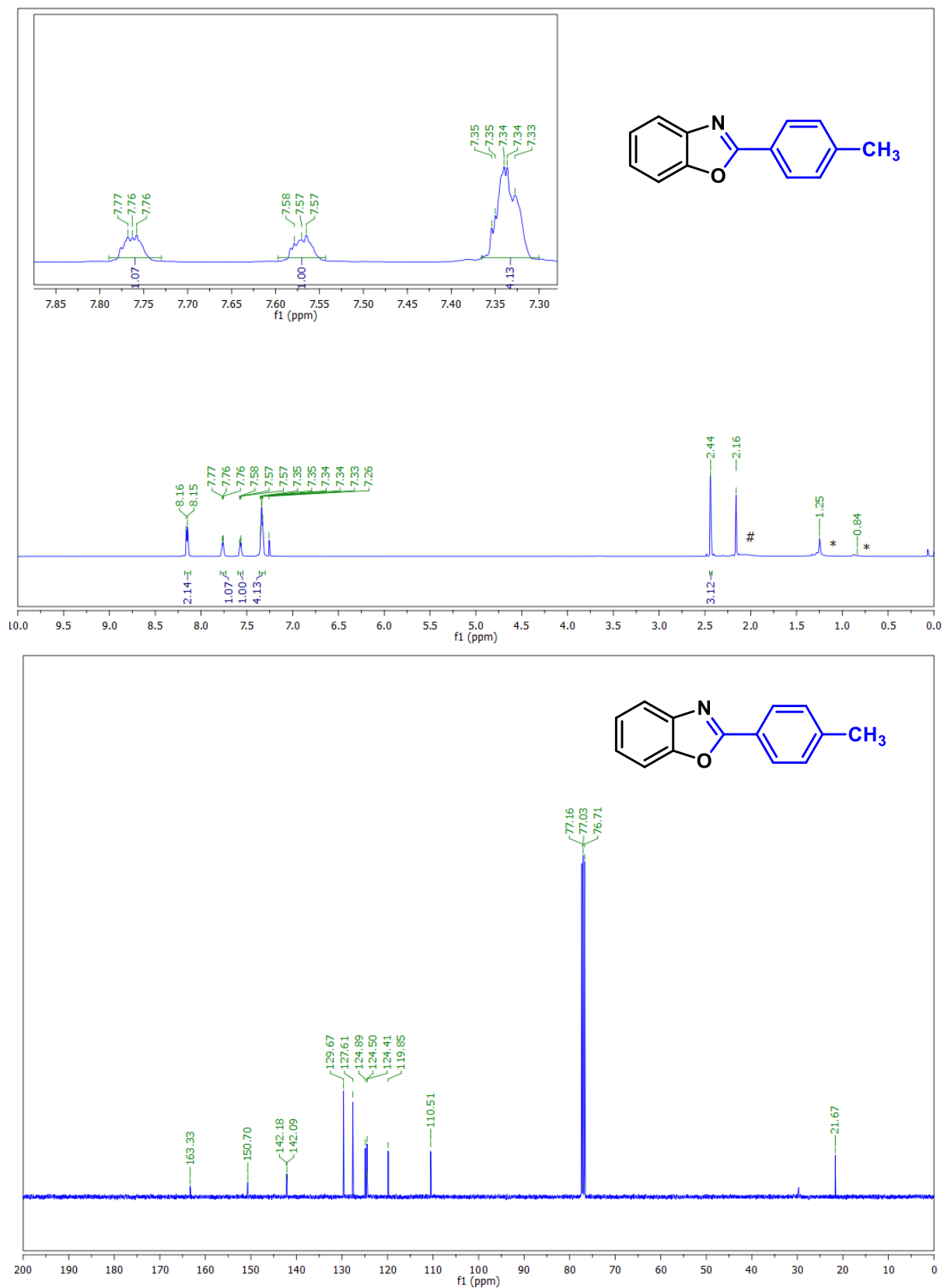
**Fig S48.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **12d** (in CDCl<sub>3</sub> solvent) (\*hexane, <sup>x</sup>water).



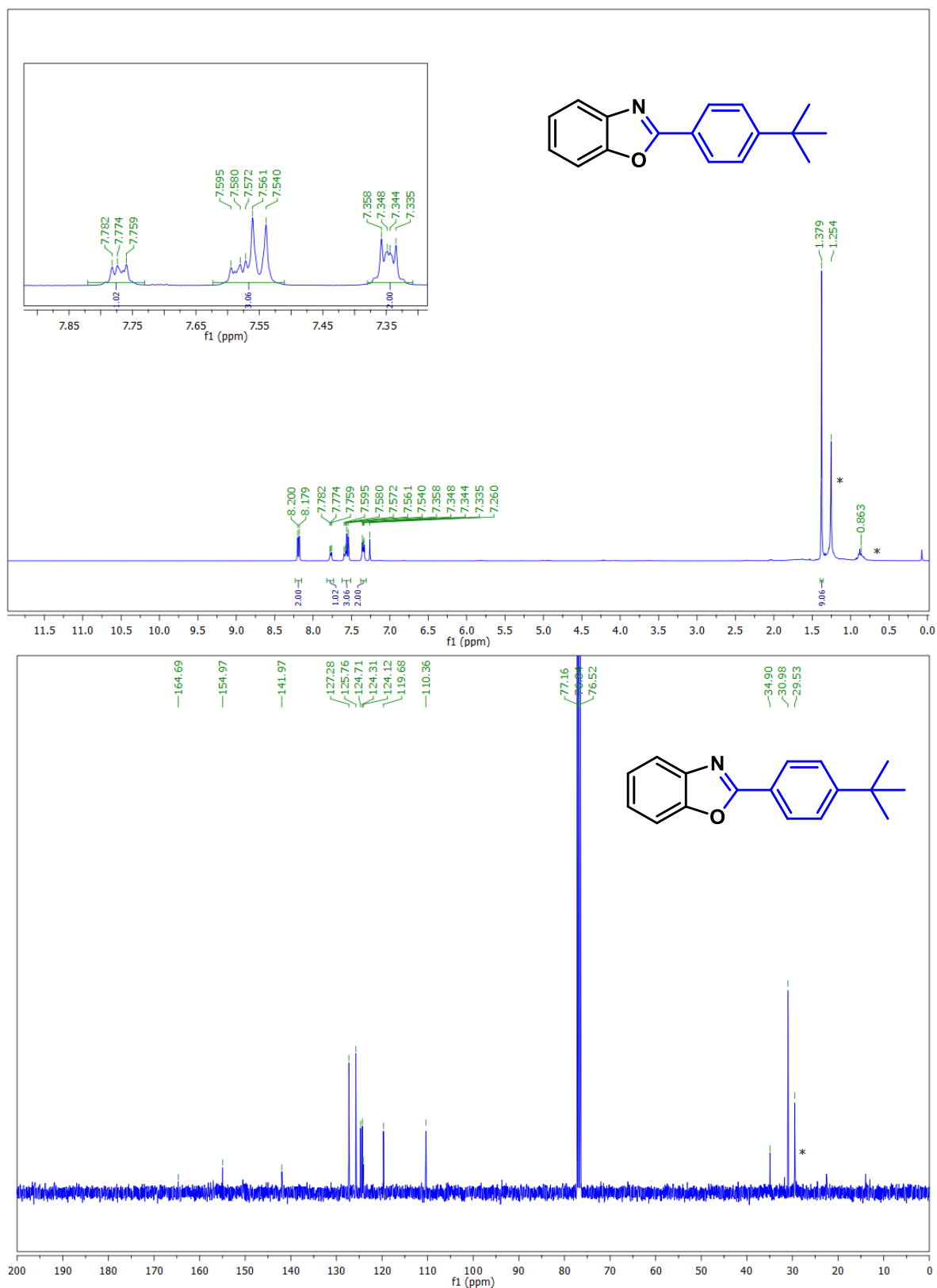
**Fig S49.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **12e** (in CDCl<sub>3</sub> solvent) (\*hexane).



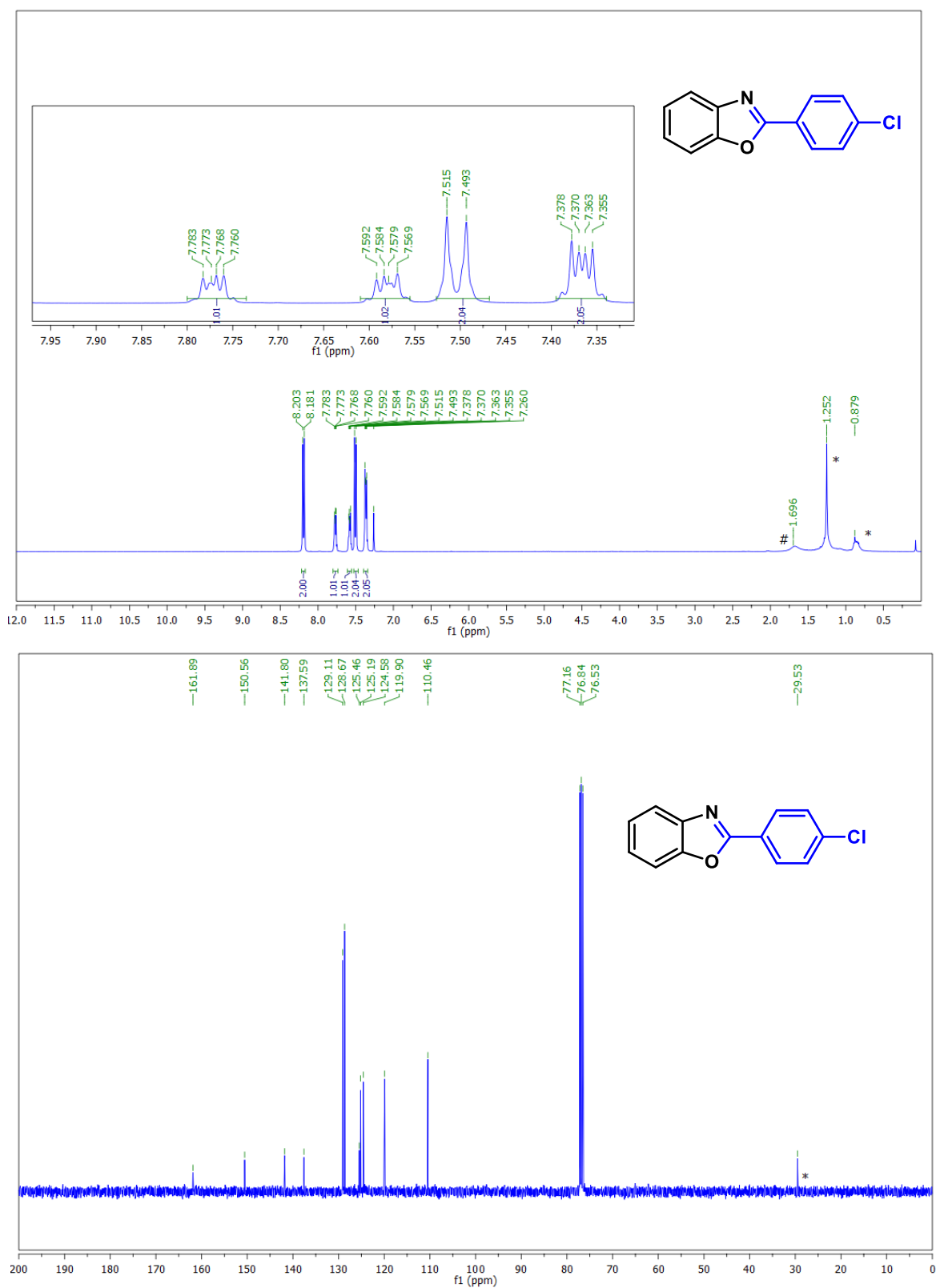
**Fig S50.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **13a** (in CDCl<sub>3</sub> solvent) (#water, \*hexane).



**Fig S51.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **13b** (in  $\text{CDCl}_3$  solvent) (#acetone, \*hexane).

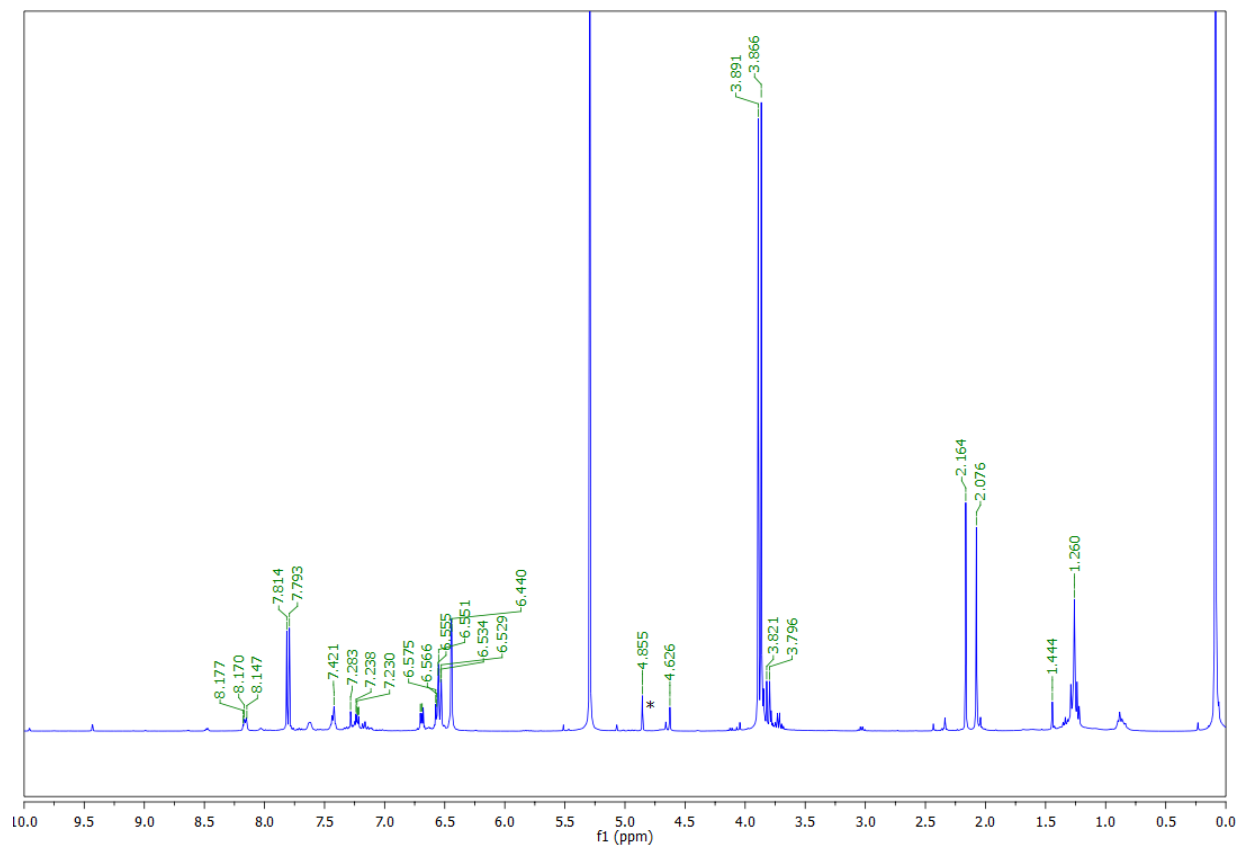


**Fig S52.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **13c** (in CDCl<sub>3</sub> solvent) (\* hexane).

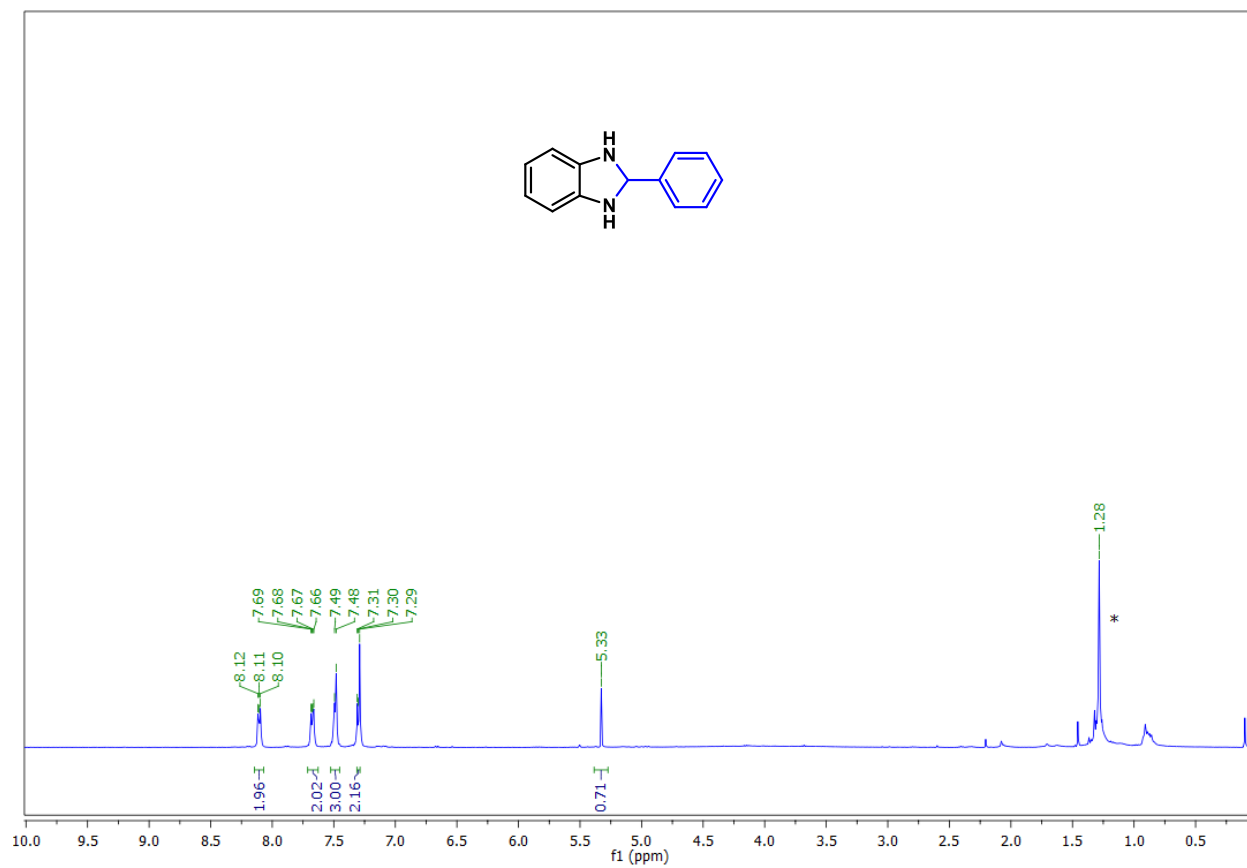


**Fig S53.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **13d** (in CDCl<sub>3</sub> solvent, #water, \*hexane).

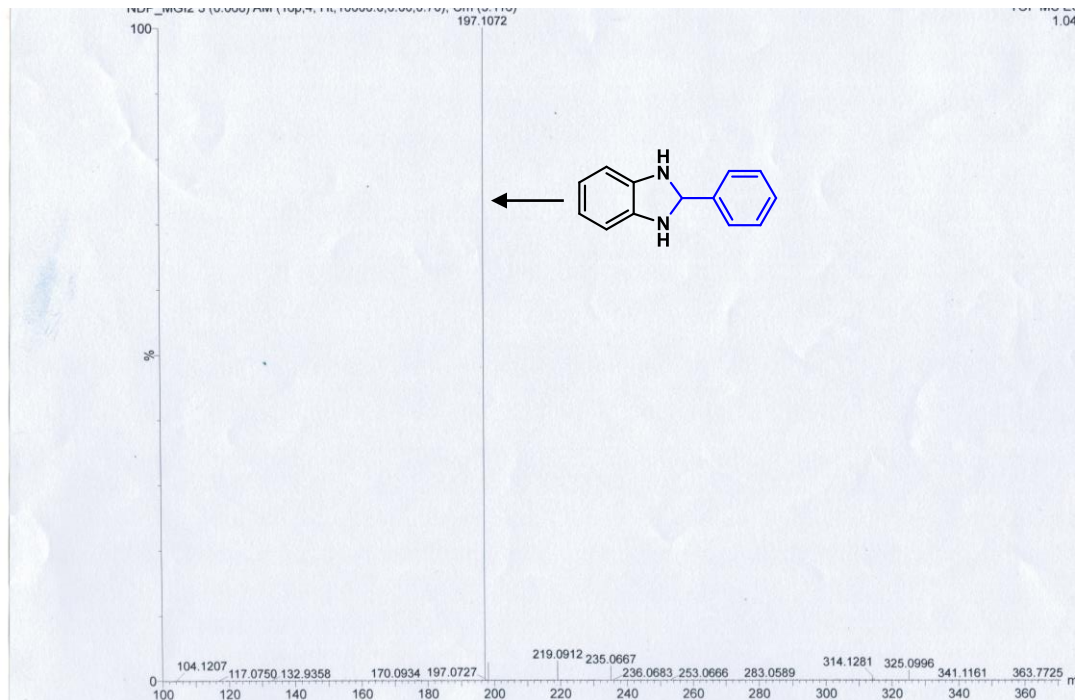




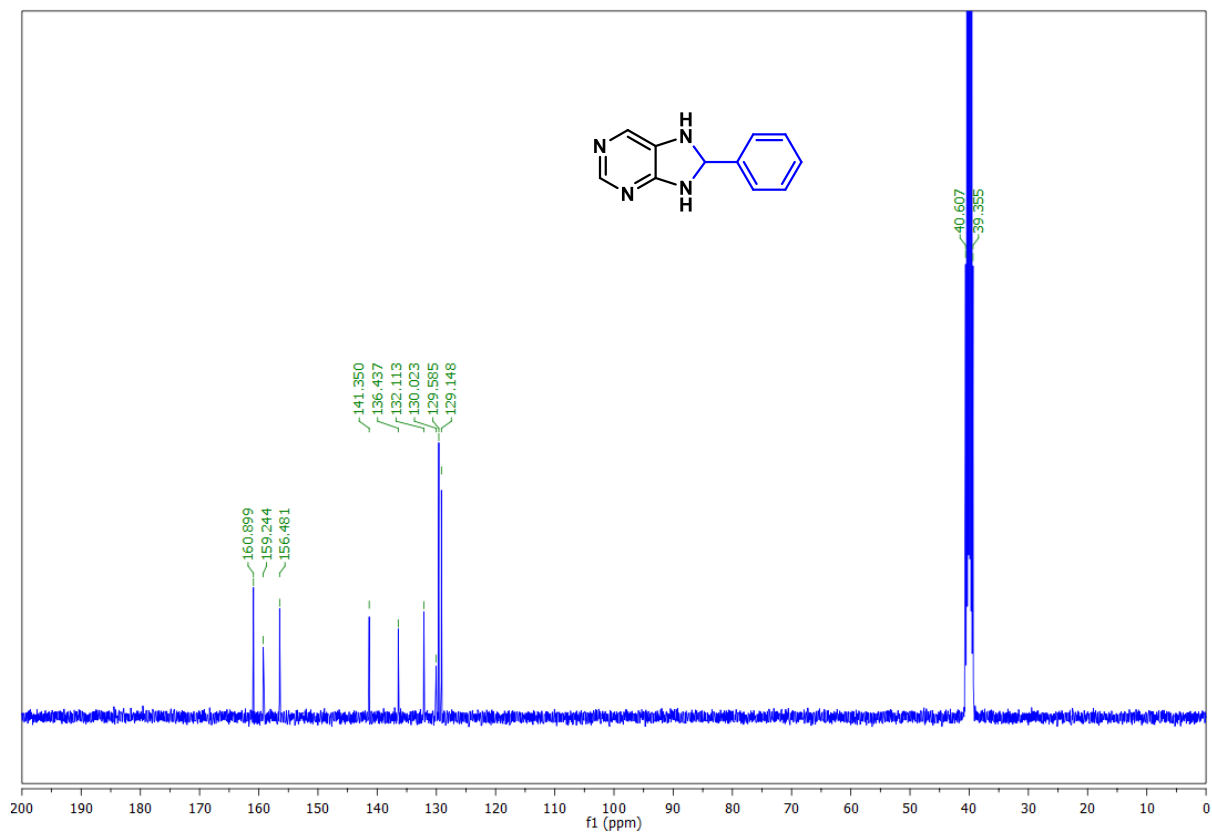
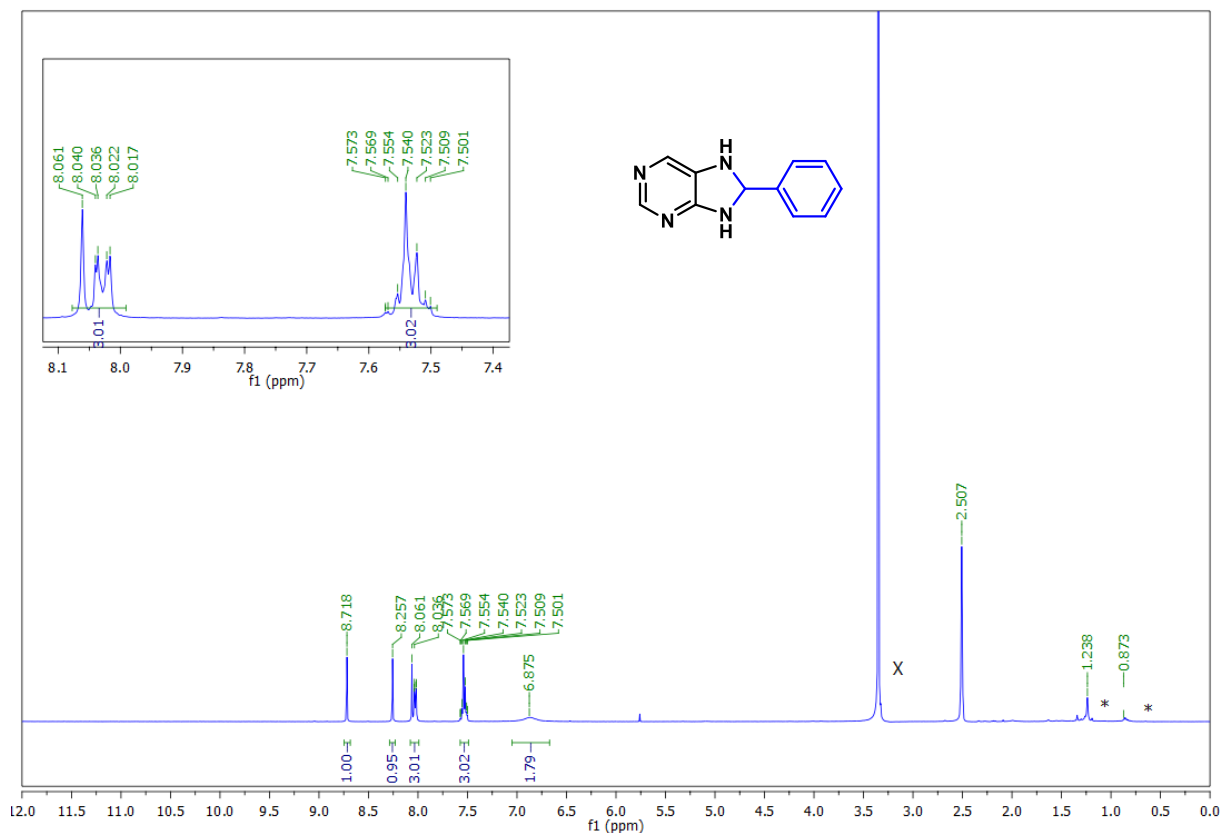
**Fig S54.** <sup>1</sup>H NMR spectrum of reaction mixture (in CDCl<sub>3</sub> solvent) (\* 2,4-dimethoxybenzyl alcohol)<sup>1</sup>



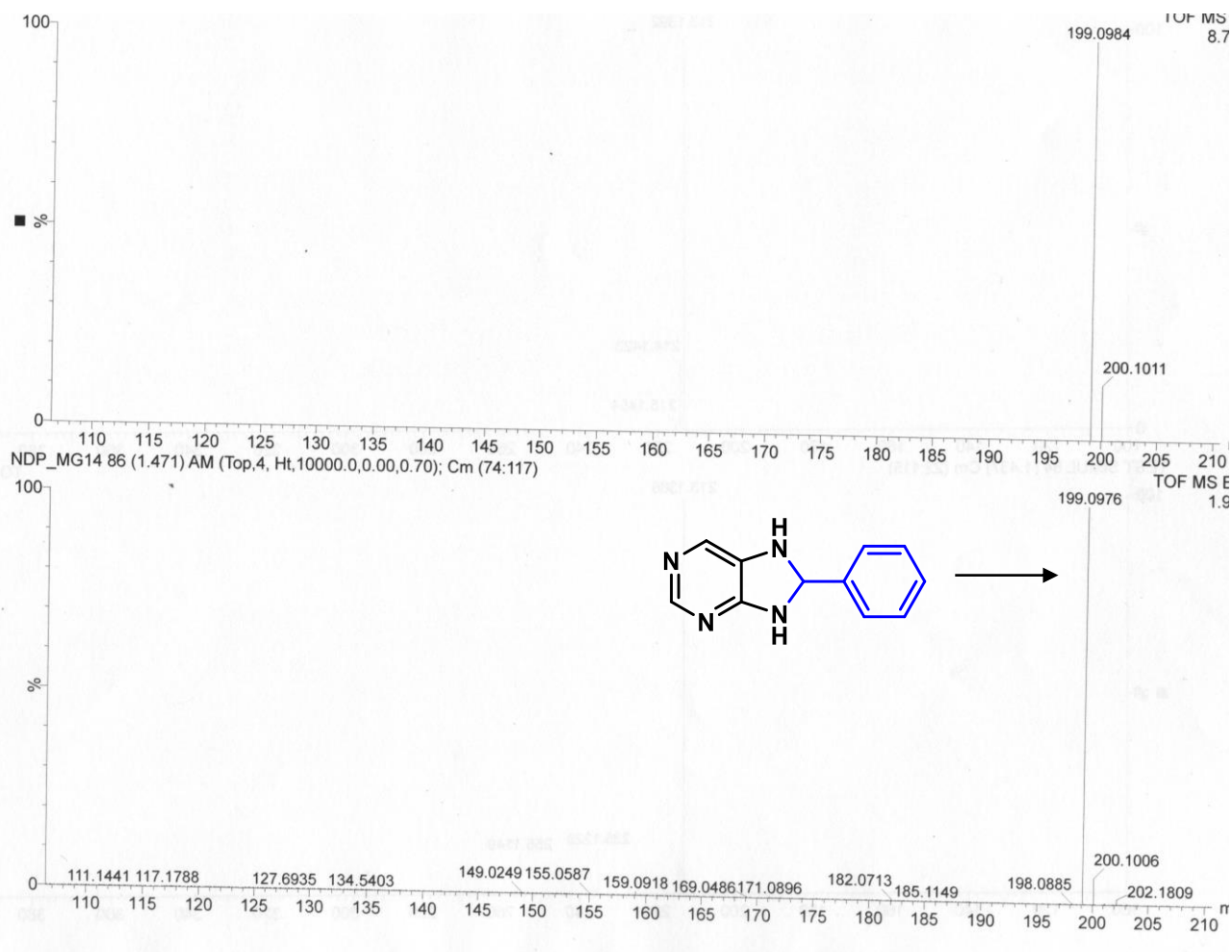
**Fig S55.**  $^1\text{H}$  NMR spectrum of **5a'** (in  $\text{CDCl}_3$  solvent) (\* hexane)



**Figure S56.** ESI-MS spectrum of  $[\text{C}_{13}\text{H}_{13}\text{N}_2]^+$  ( $[\mathbf{5a}' + \text{H}]^+$ ).



**Fig S57.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of 10a' (in DMSO-d<sub>6</sub> solvent) (X water, \*hexane).



**Figure S58.** ESI-MS spectrum of  $[C_{11}H_{11}N_4]^+$  ( $[10a^+ + H]^+$ ).

## References.

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